International Library of Technology

322B

Manufacture of Leather and Soap

74 Illustrations

Prepared Under Supervision of

HERBERT WINKEL, B. S.

DIRECTOR, SCHOOLS OF THEORETICAL AND APPLIED CHEMISTRY

INTERNATIONAL CORRESPONDENCE SCHOOLS

MANUFACTURE OF LEATHER

By ALLEN ROGERS, Ph. D.,

PRATT INSTITUTE, BROOKLYN, N. Y.

MANUFACTURE OF SOAP

By LINCOLN BURROWS,

MANUFACTURING CHEMIST

Published by

INTERNATIONAL TEXTBOOK COMPANY

SCRANTON, PA.

1924

Manufacture of Leather, Parts 1, 2, and 3: Copyright, 1902, 1909, 1922, by International Textbook Company.

Manufacture of Soap, Parts 1, 2, and 3: Copyright, 1902, 1909, 1923, by International Textbook Company.

Copyright in Great Britain

All rights reserved

Printed in U. S. A.

Press of
International Textbook Company
Scranton, Pa.
322B

86279

PREFACE

The volumes of the International Library of Technology are made up of Instruction Papers, or Sections, comprising the various courses of instruction for students of the International Correspondence Schools. The original manuscripts are prepared by persons thoroughly qualified both technically and by experience to write with authority, and in many cases they are regularly employed elsewhere in practical work as experts. The manuscripts are then carefully edited to make them suitable for correspondence instruction. The Instruction Papers are written clearly and in the simplest language possible, so as to make them readily understood by all students. Necessary technical expressions are clearly explained when introduced.

The great majority of our students wish to prepare themselves for advancement in their vocations or to qualify for more congenial occupations. Usually they are employed and able to devote only a few hours a day to study. Therefore every effort must be made to give them practical and accurate information in clear and concise form and to make this information include all of the essentials but none of the non-essentials. To make the text clear, illustrations are used freely. These illustrations are especially made by our own Illustrating Department in order to adapt them fully to the requirements of the text.

In the table of contents that immediately follows are given the titles of the Sections included in this volume, and under each title are listed the main topics discussed.

International Textbook Company

CONTENTS

NOTE.—This volume is made up of a number of separate Sections, the page numbers of which usually begin with 1. To enable the reader to distinguish between the different Sections, each one is designated by a number preceded by a Section mark (§), which appears at the top of each page, opposite the page number. In this list of contents, the Section number is given following the title of the Section, and under each title appears a full synopsis of the subjects treated. This table of contents will enable the reader to find readily any topic covered.

MANUFACTURE OF LEATHER, § 22, § 23

§ 22

Pages

Heavy, or Firm, Leathers 1–45

Introduction 1– 3

Definitions and classification; Hide structure.

Treatment of Hides 4–18

Soaking; Cold-sweat system; Warm-sweat system; Liming; Unhairing and fleshing; Leidgen unhairing machine; Deliming; Plumping the hides.

Sole-Leather Manufacture 19–45

Methods of tanning; Oak leather; Oiling and drying; Rolling; Treatment of the hides; Bleaching; Union leather; Quick sole-leather tannage.

§ 23

Heavy, or Firm, Leathers—Continued 1–42

Sole-Leather Manufacture—Continued 1– 3

Oak-tanned belting leather; Harness leather.

Vegetable Tanning Materials 4–21

Classification of tannins; Wood and bark extracts; Ott bark mill; Williams' patent bark shredder; Vat leaching.

Analysis of Tanning Materials 22–35

Analysis of bark, wood, etc.; Teas percolator extractor; Determination of non-tannins; Analysis of tanning extracts; Analysis of tan liquors.

Analysis of Leather 36–42

Determination of moisture; Determination of ash; Determination of oil; Determination of nitrogen; Determination of water-soluble materials; Determination of glucose.

Limp, or Light, Leathers 43–96

Process of Manufacture 43

MANUFACTURE OF LEATHER—(*Continued*)

Pages

Automobile and Upholstering Leathers 44–51
Stoning jack; Splitting machines; Daubing; Embossing.

Bag, Case, and Strap Leather 52–59
Stuffing materials; Hand and drum stuffing; Fat-liquoring; Whitening.

Side Leathers 60–62

Shoe, Glove, and Fancy Leather 63–68
Working out skins; Shaving; Staking; Seasoning; Surfacing.

Vegetable-Tanned Calfskins 69–71

Vegetable-Tanned Sheepskins 72–73

Hogskins 74

Tawing 74–76

Oil Tannage 77–79

Chrome Tanning 80–89
Two-bath chrome-tanning process; One-bath chrome-tanning process; Fat-liquoring; Box calf; Matt calf; Glazed kid; Chrome patent leather.

Dongola Leather 90–91

Leather Dyeing 92–93

Measurement of Leather 94–96

MANUFACTURE OF SOAP, § 24, § 25, § 26

§ 24

Introduction 1– 3
Definition of soap; Classes of soap; General outline of the manufacture of a settled soap.

Raw Materials of Soap Manufacture 4–63

Animal Soap Stock 4– 5

Manufacture of Animal Soap Stock 6– 7

Vegetable Soap Stock 8–27
Cottonseed oil; Cocoanut oil; Palm-kernel oil; Corn oil; Olive oil; Red oil; Lime-saponification process; Acid-saponification process; Aqueous-saponification process; Twitchell process; Rosin.

Alkalies and Their Manufacture 28–49
Le Blanc process of manufacturing sodium carbonate; Solvay process; Castner electrolytic process for the production of caustic soda and chlorine; Grading of soda ash; Grading of caustic soda; Preparation of caustic-soda lye; Caustic potash; Measurement of the density of liquids.

MANUFACTURE OF SOAP—(*Continued*) *Pages*

Chemistry of Soap Manufacture..... 50
Glycerides and Their Properties..... 50–53
Behavior of Fats and Oils Toward Saponifying Agents 54–63

§ 25

Processes of Soap Manufacture..... 1–65
General Remarks 1
Manufacture of Boiled or Settled Soaps..... 2–54
Boiling-room processes; Soap kettle; Stages of saponification; Graining the soap; Rosin changes; Filling the soap; Crutching the soap; Soap pumps; Filling materials; Finishing-room processes.
Semiboiled Soaps 55–57
Cold-Process Soap 58–65

§ 26

Remelting of Soap..... 1– 3
Manufacture of Toilet Soap..... 4–21
Milled-Process Soap 4–16
Perfuming of Soap..... 17–18
Coloring of Toilet Soap..... 20–21
Manufacture of Soap Powder..... 22–24
Recovery of Glycerine From Waste-Soap Lye..... 25–41
Manufacture of Glycerine..... 25–32
Treatment of Crude Glycerine..... 33–41
Chemical Examination of Raw Materials and Products 42–69
Examination of Soap Stock..... 43–57
Sampling; Titer test; Wijs method for determination of iodine value; Analysis of rosin; Analysis of soda ash; Analysis of commercial caustic soda.
Routine Chemical Examination of Kettle-Room Products 58–63
Analysis of waste soap lye; Acetin method; Bichromate oxidation method.
Soap Analysis and the Interpretation of Results..... 64–65
Chemical Examination of Refined Glycerine..... 66–68
Specifications for Glycerine..... 69

MANUFACTURE OF LEATHER
(PART 1)

HEAVY, OR FIRM, LEATHERS

INTRODUCTION

1. Definition and Classification.—The term **leather** is applied to the product obtained by the treatment of hides or skins of animals with certain reagents that convert the animal tissues into a tough, opaque, pliable, and fibrous substance which is not subject to putrefaction.

2. The pelts of animals come to the tanner in four conditions: *green* or *market* (fresh from the animal); *green salted* (when salt has been rubbed on the flesh and the skins placed in piles to cure); *dry salted* (same as green salted but afterwards allowed to dry); *flint,* or *dry, hides* (usually stretched and allowed to dry in the sun). According to their size, these pelts are divided into three general classes, namely, *hides, kips,* and *skins.* **Hides** comprise the coverings of larger animals such as the cow, horse, camel, and walrus. These are used for heavy leather manufacture such as shoe soles, machinery belting, harness, and other purposes where stiffness and strength are required. They are also often split for the purpose of producing shoe leather, bag, case, strap, automobile, and furniture leather. **Kips** are the undersized animals of the same species. **Skins** are obtained from small animals such as sheep, goats, and calves. Kips and skins are used in the

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

manufacture of light leather for shoe uppers, pocketbooks, bookbinding, gloves, and fancy articles. Both hides and skins are graded according to weight and imperfections, the latter being in the nature of cuts, brand marks, hair slips, and grubs. Diseased hides are some times found and are a source of great danger to the tanner.

3. Hides are obtained from the various slaughter houses over the country and are known as *domestic,* or *native.* They are also obtained from other parts of the world and are usually known by the name of the country from which they originate.

HIDE STRUCTURE

4. Analysis of Skins.—At first glance, the pelts of various animals appear to have little in common. On closer examination, however, a very close similarity will be observed. In structure, all animal skin is made up of several readily defined layers. The skin is not merely a covering for the animal, but also serves as a container for nerves and secretive glands, and as a bed, or ground, for the hair, or fur. It is made up of two principal layers: the *epidermis,* or *cuticle,* and the *corium,* or *true skin.* These two layers are totally distinct in structure, origin, and functions.

5. The **epidermis** is a thin covering of the true skin and is entirely removed before the tanning operations begin. In life, the upper, or external, part is being constantly worn away, falling off in the form of dry scales. The interior part of the epidermis is made up of numerous living nucleated cells; as the surface of this layer is reached, these cells become flattened and finally dry up and form the exterior part of the epidermis and ultimately drop off as dead scales. These cells, which renew the horny external tissue of the epidermis, are in turn renewed by vessels situated in the corium, or true skin. The epidermis does not combine with tannin and is therefore removed, laying bare the true skin, which is known to the tanner as the *grain.*

6. The **corium,** or *true skin,* is the skin with which the tanning agents combine to form leather. There is an intermediate albuminous layer between the corium and the epidermis. Both layers are composed of interlaced bundles of fiber running across and above one another and parallel to the surface of the skin. These fibers are surrounded by fluid matter, which serves to keep the skin in a moist and pliable condition. On removal of this fluid the fibers alone remain, and if dried by a gentle heat they assume a horny appearance and become in substance about one-third of the raw hide.

The corium determines the quality of the leather that can be made from a hide. Its thickness, flexibility, and strength are reproduced in the leather. Between the fibers of the corium is an albuminous substance called **coriin:** in a dry state this holds and connects the fibers.

The connective tissue of the corium gives form to the skin, the intercellular substance, coriin, lying between the fibers. When boiled with water, these connective tissue fibers form glue, losing their organized structure, and making a homogeneous jelly.

7. The intercellular substance is probably a decomposition product of the connective tissue. This coriin is soluble in lime water and other alkaline solutions; frequent treatment of the skin with these reagents withdraws fresh quantities of soluble matter with every treatment. This fact should be noted in connection with the liming of skins to remove the hair.

Dilute inorganic acids swell the connective tissue. The swelling of the skin by acids is made use of to facilitate tanning; it not only makes the skin more sensitive for the reception of the tanning material, but also effects the disintegration of the fiber bundles into individual fibers, thereby increasing the surface.

8. The **under skin** is made up of loose connective tissue, embedded in which are the sweat and fat glands, the blood vessels, and muscular fiber. Fig. 1 shows an enlarged microscopic transverse section of the skin in which the Malpighian net, or lower layer of the epidermis, is shown at *d*; the corium,

at *b*; the lobules of adipose tissue, at *m*; the external orifices of the sweat glands, at *a′*; a hair follicle, at *y*; a shaft of hair in the hair follicle, at *z*; a hair papilla, at *i*. At *l* is illustrated the connective tissue of the under skin, showing the sweat glands *a*, with the ducts *c*, through which the sweat passes to the surface of the skin; at *k* is shown a hair bulb, and at *e* are shown openings of the sebaceous glands. The horny outside layer of the epidermis *h* shows hair, as at *f*, or wool at different places. The hair is not embedded immediately in the surface, but in the capsules, or sacs, being continuous with the epidermis and reaching down to the corium.

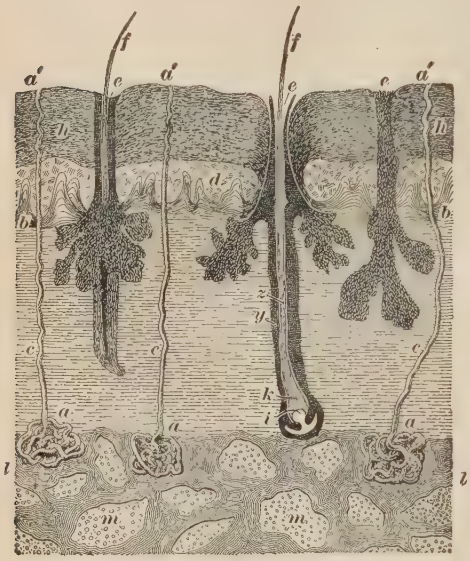


Fig. 1

TREATMENT OF HIDES

9. Some operations in the manufacture of leather are followed, with more or less variation, in all branches of the industry, and, to save repetition, these will be treated generally, variations being noted in descriptions of the tanning processes necessary for the production of specific kinds of leather. These variations are so numerous that it will be impossible to enumerate them all, but enough will be noted to indicate what latitude exists in the application of the general principles involved.

10. Soaking.—Whatever may be the class of hide in use at the tannery, the first operation is that of soaking.

This is always done by means of water, with or without the addition of chemicals. The various kinds of hides require different treatment as to mechanical handling, character of the soak, and the duration of the soaking. Whether the hide is *green* or has been dried with preservatives (in this case these preserving agents must be washed out), the dirt, blood, and dung must be removed, and the hide brought back to a state similar to that in which it was when taken from the carcass. All the foreign matter goes into the soaks, and only a short time elapses before the water becomes filthy.

Where hard water is used, it is customary to add some softening agent, as borax, soda ash, or caustic soda, since soft water is better adapted to soaking purposes. Much valuable hide substance is lost in many tanneries through the use of soaks that have become putrid. An old soak gives better results than a new one, but if the vat is allowed to become putrid, depletion of the hide takes place, and the loss from this cause more than offsets the time gained. Plenty of pure water with a little borax or soda, if needed, is a much more effectual cleanser and softener than a putrid liquor.

11. The general form of receptacle for the soaking is a pit or vat sunk in the ground. Wheels or drums have been used, and in some places are still employed, but the ordinary vat is the most convenient receptacle for the purpose. The hides are either hung in the water on racks or thrown in and spread out. Dried hides are generally placed in piles in the pits and the water then run on them.

While in the soaks the hides must be watched by skilled workmen so that they will not become putrid. Thin hides must be removed as soon as they become soft, without waiting for the thicker ones to soften. The thin parts of all hides must be carefully watched, in order that they will not become damaged while the heavier parts are softening.

12. Hide Mills.—Where heavy hides are being made into sole leather it is customary to use **hide mills,** also known as *kickers,* or *stocks.* A hide mill is merely a heavy iron shoe on the end of a vertical beam keyed at the other end. A

backward-and-forward motion is imparted to the beam by a heavy shaft and the shoe moves in a heavy receptacle containing the hides. The hides are kept constantly in motion in contact with running water, and a couple of hours of this treatment is more beneficial than a day's quiet soaking. The hides are first put in the soaks until they become softened, and the mills are then used to finish the operation. Similar, but lighter, mechanical contrivances are used for the same purpose where lighter pelts are treated.

Many tanners run the partly softened stock in a drum. Here the tumbling action helps materially to hasten the softening. For green-salted hides it has also been found advantageous to do away entirely with pit soaking, simply depending upon milling the stock in the drum in the presence of running water.

13. Depilation.—Having brought the stock to a soft and clean condition, the next step is to remove the hair and epidermis, the operation being known as *depilation.* This may be accomplished in several ways, the oldest of which is known as *sweating.* Sweating may be carried out either in a cold or warm pit or cellar and is termed *cold sweat* or *warm sweat.* In both cases the results secured are due to incipient putrefaction.

14. Cold-Sweat System.—As used in the United States, the cold-sweat system is carried out as follows: The sweat pits are vaults built of stone, with the proper apertures for ventilation, in order to regulate the temperature. Tight doors are provided, and these may also be used for ventilating purposes. After the hides are thoroughly soaked and softened, they are hung over poles or suspended by the edges in the sweat pit. The doors are closed until the putrefaction begins, and when this takes place careful watching is necessary. The hides are carefully scrutinized, and those in which the putrefaction is far advanced must be removed at once. The presence of a hide in the sweat pit for even a few hours after it is ready to come out, may spoil it.

The sweating process hastens the expansion of the hide, opens the pores, and brings the hide back to a state analo-

gous to that at the time of slaughter; it gives to the dry, wild hide a much-needed development. During the putrefaction process much ammonia is generated as a result of decomposition. Efforts are being made to isolate the specific germ causing the putrefaction that loosens the hair. If these efforts are crowned with success and an antiseptic is found that will be fatal to germs other than those which cause putrefaction, the sweating process will be greatly simplified.

After sweating, the hides are thrown into water or a weak lime bath, which stops further putrefaction.

15. Warm-Sweat System.—As practiced in Germany, the warm-sweat system consists in placing the folded hides in an air-tight buried box, which is then covered with spent tan. Steam is frequently used to accelerate the sweating process, but its use is attended with great risk; the heat spontaneously generated by the hides is preferable. This system requires even more care than the cold-sweat process, because putrefaction promoted by heat makes rapid progress and may cause great loss.

*If fresh-slaughtered hides are to be depilated by the sweating process, the flesh side must be thoroughly salted and the hides then folded; they are piled one on another and covered with straw. They are taken down after 18 or 20 hours, the hides opened and refolded, and again piled and covered, after which only occasional turning is needed to make the hair begin to slip. In the United States, most of the fresh-salted hides are limed and not sweated.

16. Liming.—The depilation of hides is most commonly accomplished by placing them in a solution of lime until the hair bulb is loosened, when the hair can be readily scraped off. The lime acts on the roots of the hair and the hair sheaths are dissolved, but the hair itself is but slightly altered. Lime also acts on the skin; the fibers swell and absorb water, so that the skins become plump and swollen, and at the same time the substance that glues the fibers together is dissolved

*In the United States the warm-sweat system differs from cold sweat only in regard to the temperature of the sweat pit.

and the skins become a mass of finer fibers. The lime also saponifies the natural fat, or oil, of the skin.

17. Lime vats are made of timber or of masonry and are sunk into the ground so that the tops of the vats are on a level with the floor. The contents of the vats are made up by slaking the desired amount of quicklime and thoroughly plunging the solution. Generally, two or more lime vats of different ages are used, the hides remaining in one vat for a time and then being moved by means of hand reels between the vats, to the next lime vat.

The time required for liming depends on the kind and condition of skins, conditions of the atmosphere, and the temperature of the limes in use.

The question of when to throw away the limes is also an open one. Some tanners use them until they are almost saturated with decomposing matter extracted from previous hides. A lime in this state becomes a depilator by means of putrefaction and not because of its caustic action, but this should not be considered as good practice.

18. Lime in excess must be present in the vats, so that a saturated solution of the hydrate of calcium is always surrounding the hides. Lime in solution is rapidly consumed in the depilation of the hides and must be constantly renewed. Much of the residue of the lime vats, generally mistaken for unused lime, is in reality a mixture of calcium hydroxide and calcium carbonate formed during the liming process. It is, therefore, found practical to add fresh lime from time to time to the vats and by frequent plungings keep it in suspension.

19. Hydrated Lime.—In place of the older method of using lump lime, many tanners now employ the product known as *hydrated* lime. This form of lime is produced by adding just sufficient water to bring about the union between the calcium oxide and water, according to the following reaction

$$CaO + H_2O = Ca(OH)$$

The advantage of this material, which comes to the tanner in the form of a powder packed in bags, is that it may be kept indefinitely without change, and is always uniform in composition and action.

20. Sodium Sulphide.—Sodium sulphide, when dissolved in water and used as a depilating agent, has the property of quickly destroying hair and epidermis. It has the advantage of rapid action and the production of a tight leather, but has at the same time the disadvantage of a tendency to cause a drawn condition of the grain. For certain classes of leather, its use is desirable, in which case a 20° Bk.* solution is prepared in a paddle at a temperature of 70° F. The stock is entered and the paddle run for about 2 hours, when the wheel is stopped and after that it is run for 5 minutes each hour during the remainder of the day. The stock is kept in the liquor overnight and turned from time to time during the morning. At about noon the plug is drawn and the spent liquor discharged. The paddle is filled with water and run for half an hour. One per cent. of sodium bicarbonate is now added and the wheel turned for the same length of time. Fresh water is then turned on and the stock washed in running water for 3 hours.

Sodium sulphide is sometimes used with lime. It forms caustic soda and calcium sulphide when it comes in contact with the lime. The calcium sulphide acts as a solvent for the hair and renders easier the removal of the very fine hair. The use of sodium sulphide shortens the unhairing process and causes less loss of hide substance as compared with lime, but it has the disadvantage of causing brittle, harsh leather unless it is carefully used in comparatively small amounts. The usual custom is to add the sodium sulphide in the first stages of depilation, the amount employed being about 10 per cent. of the lime taken.

21. Sodium Sulphide and Calcium Chloride.—It has been found that a combination of calcium chloride with

*See *Manufacture of Leather,* Part 2.

the sodium sulphide will obviate the danger from drawn grain and the process is carried out as follows: Into the paddle is placed a weighed amount of sodium sulphide sufficient to produce a 20° Bk. solution. To this solution is added 1 pound of calcium chloride for every 4 pounds of sulphide taken. The same method of handling is pursued as for straight sulphide, except that 2 per cent. of sodium bisulphite is used for neutralization in place of sodium bicarbonate.

22. Arsenic sulphide is sometimes used in connection with lime and has the advantage that it does not produce a strong caustic condition. The form of arsenic sulphide employed is that known as realgar, or red sulphide of arsenic, having the formula As_2S_2.

23. Unhairing and Fleshing.—After the liming or sweating operation is completed, the hides are ready to have the loosened hair scraped off and to have the fleshy and fatty matter on the flesh side removed. These operations are known, respectively, as *unhairing* and *fleshing*.

The unhairing and fleshing of hides is done both by hand and by machine. The latter method is superseding the hand method only slowly, because of the care needed in operating the machine. An unskilful or careless operator may spoil hundreds of dollars' worth of hides in a day's work, and the greatest care and judgment must be exercised on the part of the workman while running the machine.

The operations of unhairing and fleshing take place in what is known as the *beam house*. After the hair has been loosened, the hides are brought into the beam house; if the sweat pit has been used to loosen the hair, the hides are placed in cold water, which cools them and interrupts the putrefaction that has set in. Limed stock is generally unhaired without previous washing, being brought directly from the limes to the beam house.

24. The beams on which the hand process of unhairing takes place are convex in shape, one end resting on the ground while the other is about the height of the workman's waist.

Over these sloping beams the hides are spread and by means of a concave knife, the curvature of which conforms to that of the beam, the hair is removed. The operation is fatiguing, and only men of long experience, skill, and considerable strength, are employed.

The knife is pushed against the hair, the sides being worked from the hind shank toward the head and then toward the back. In removing the short, fine hair, hides are occasionally damaged by having the grain cut; to prevent this, a guard that projects beyond the edge of the knife and serves to protect the hide, is sometimes used. After the hair is removed, the hides are placed in water overnight and are then usually ready for fleshing.

25. The operation of fleshing by hand consists in removing the fleshy and fatty matter by means of a sharp knife. The work requires great skill. Both straight and curved knives are used in the operation. The hide is thrown across the beam, which has first been covered by a hide already fleshed. The flesh is removed by long strokes of the knife, held in a slanting position, the right hand being uppermost. A long, steady drive results in fewer accidents to the hide than a short, choppy stroke. After the flesh has been removed from the main body of the hide, the hide is trimmed with a sharp knife and the shreds and projecting filaments are removed. All the fleshings are saved and sold for glue making.

After fleshing, the hides are hung on individual sticks in vats of fresh water. If the hides are to be used for upper leather, the soaking is dispensed with and the hides at once bated.

The hand method of fleshing and unhairing is slow, and has been almost entirely superseded by machines, which, if placed in the hands of skilled operators, do the work for about one-third of the former cost.

26. Machine Fleshing and Unhairing.—With machinery, the hides are fleshed either after soaking and before liming or after they come from the limes. If fleshed before liming, they are generally run through the machine again after

coming from the limes, in order to remove both the flesh left on after the first fleshing and the flesh raised up by the liming process.

The machines that do the beam-house work are heavy, rigid affairs. The removal of the hair and flesh is accomplished by rapidly revolving rolls, having raised irregular spines on their surface.

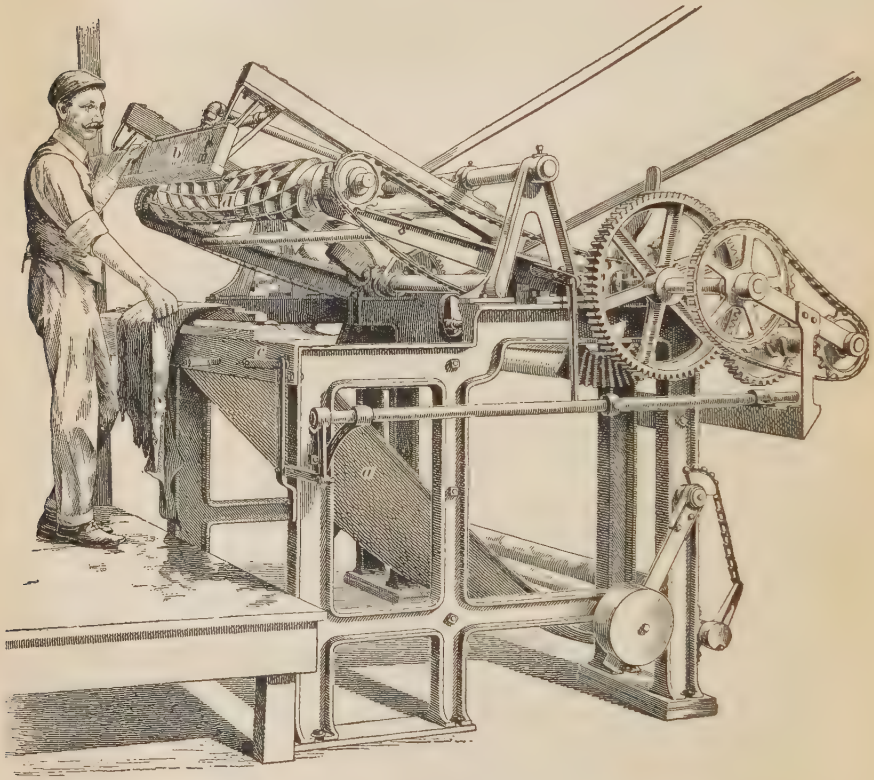


Fig. 2

27. The **Leidgen unhairing machine,** Fig. 2, is an approved machine for unhairing. It consists of a revolving cylinder *d* supported on a steel frame that moves up and down in the arc of a circle, at the will of the operator, over a flexible bolster *a* on which the hide to be dehaired is placed.

The hide or side is thrown flat on the flexible bolster *a*, the holder *b* is brought down and automatically clamps the end of the hide or side. The lever *c* is then thrown so as to put the machine in operation. The cylinder *d*, revolving at the rate of 190 revolutions per minute, moves down and up over the hide spread on the flexible bolster *a*. By reversing the lever, the revolving cylinder may be made to travel up and down within the space of 2 or 3 inches. After the hair is removed from one end of the hide, the holder is released, the position of the hide on the bolster reversed, the holder again brought down and the remainder of the hair removed. Jets of water from a perforated pipe running behind the holder constantly play on the hide while it is being dehaired.

The cylinder *d* is of cast iron, 6 inches in diameter, on the surface of which steel blades are inserted. The cylinder always revolves in the same direction whether passing up or down over the hide. The bolster *a* is securely fixed at the upper end and suspended at an angle of 45°; at the lower end, by a system of weights and levers, an equal tension is produced at all times over the entire surface. Being supported only at the ends, the bolster is perfectly flexible over its entire surface, and the thick and thin parts of the hide are thereby subjected to even pressure. This machine will perform the work of 6 men and, with a skilful operator, there is little danger of damage to the stock.

28. For removing the flesh from the hide, the fleshing machine, shown in Fig. 3, is largely used in the tanneries of the United States. It consists essentially of a spirally bladed fleshing roll *a*, past which the hide is fed by a rubber-covered bed roll *b* working in connection with a pair of fluted steel grip rolls *c* and *d*.

The illustration shows the fleshing machine with grip rolls open, ready to receive the hide or side to be fleshed. The operator inserts the hide flesh side up between the parted rolls. A slight pressure on the treadle *e* causes the grip roll *c* to move down through the circular guides and take its place between the grip roll *d* and the rubber roll *b*. All three rolls

move forward, thus firmly gripping the hide and holding it in the proper position without damaging it. The revolution of the bed roll *b* and grip rolls *c* and *d* pulls the hide between the bed roll and the rapidly revolving fleshing cylinder *a*, which removes the flesh from the hide as it slowly passes under the cylinder. When the fleshing is completed, the treadle *e* is depressed, and while the rubber and front grip rolls are moving

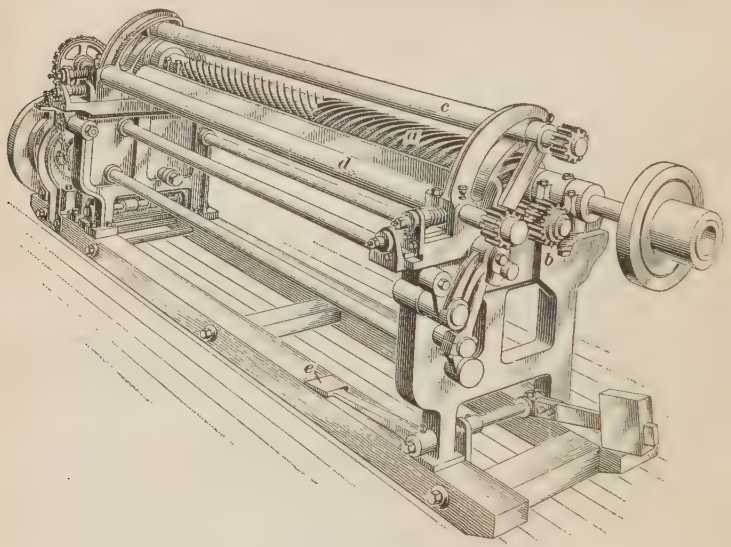


Fig. 3

away from the cylinder the middle grip roll is traveling up and back through the circular guides, and the hide is released. One-half of the hide is fleshed from the center to the end, and is then reversed and the other portion is fleshed. The thick rubber covering of the bed roll, aided by springs on which its bearings are mounted, serves to compensate for varying thicknesses of the stock being worked. Similar springs on the bearings of the front grip roll prevent undue compression of the thick parts of the hide.

29. Deliming.—It is essential that the lime or other depilating agent should be removed after it has done its work.

For sole and belting leather, it is only necessary to remove the depilating agent, but for soft leather the stock should also be brought to an open and flaccid condition, which is accomplished by what is usually spoken of as *bating* and *puering*. These two terms formerly meant two distinct processes, the former term being applied when pigeon or hen manure was used, and the latter when dog manure was employed. Today, however, the term *bating* is most generally used and *puering* only spoken of in connection with the manufacture of goatskin into leather. The use of animal excrement in recent years has been almost entirely replaced by less objectionable materials and that step in the operation placed on a scientific basis.

Ordinary deliming may be accomplished by means of weak organic acids or certain chemicals, while bating, puering, or drenching must be brought about through fermentation, or bacterial or enzyme action. As bating plays only a minor part in the manufacture of heavy leather, its consideration will be postponed until the processes involved in the production of light leather are discussed. Mention should be made, however, at this point, of some of the most important chemical deliming agents.

30. Lactic Acid.—In recent years, lactic acid has come into quite general use as a deliming agent. About 2 pounds of acid are employed for each 100 pounds of stock. This acid not only removes the lime, but, if added to the amount mentioned, has a tendency to plump the hide, which is very desirable in the production of soles.

31. Formic Acid.—Formic acid comes to the tanner as a 60 per cent. solution and is preferred by many on account of the rapidity of the action. Like lactic acid, it is also a strong plumping agent.

32. The common practice in heavy leather is, after fleshing, to wash the stock in running water and then place it in the cold pool over night, when the subsequent operations are carried out.

33. Plumping the Hides.—In making sole leather, where weight is desired, it is advantageous to secure a good degree of plumpness before the hide reaches the liquors that really do the tanning. By **plumping** is meant the swelling of the cells and the distension of the pores of the hide, so that the entrance of the tanning liquor is facilitated. If the hide becomes too plump, hard, brittle leather results; hence, it is very essential that the proper degree of plumpness is attained.

The plumping is done by acids that are either formed in the tan liquors or are added to them. The natural acids formed in a vegetable tan liquor are mostly lactic and acetic. All of them are of fermentative origin, formed by the decomposition of the sugars constituting a part of the non-tannins of the bark. The absence of the requisite amounts of non-tannins in the liquors will thus cause a scant supply of plumping acids. For this reason, several so-called *sweet tanning agents* are unfitted for tanning heavy leathers, unless they are mixed with other liquors rich in non-tannins.

Quebracho extract is a liquor in which the proportion of the tannins to the non-tannins is so great that acid is slowly formed, and a quick tannage is secured but the leather is not well filled or nourished. If quebracho is mixed with some liquor with a large non-tannin content, this difficulty is removed. The extracts made from oak or chestnut woods are great acid makers because of their high percentage of non-tannins.

34. Methods of Obtaining Plumping Acids.—In a well-regulated bark yard, the acid formed will be in the proper proportion to the tannin in the liquor, and there is no need of the addition of plumping agents. It sometimes happens, during the cold seasons of the year or when a yard is starting up after an extended shutdown, that the acid is deficient.

Various methods are employed in order to help the formation or increase the supply of acid. Crude molasses is sometimes added; a mixture of old cheese, molasses, or glucose, and some substance containing nitrogen, as ammonium nitrate, will stimulate the production of lactic acid. Commercial lactic, acetic, and formic acids are all used for plumping purposes.

The increasing percentage of extracts used for tanning is gradually causing the tanner to provide means for the development of acid in his yard, and eventually in every tannery the plumping acid will have to be added to the liquors in the form of organic acids, or *grown* in the liquors by the addition of ferments, or by the use of acid-forming tanning materials.

35. It sometimes happens that too much acid is formed in the yard. The reason for this is not easily determined. It may be due to the season or the weather; it may be caused by the method of leaching, the nature of the water supply, or it may be due to other causes seemingly too insignificant to produce such an effect. A tannery where the bark is closely leached will have more acid in the yard than the tannery where there is less regard for economical practices in the leach house. A very soft water or a peaty water will help acid production.

A yard with too much acid is harder to handle than a yard with too little acid. It requires close watching to prevent the production of hard leather inclined to crack and a consequent heavy financial loss. This condition of the yard may be only temporary, or it may be a permanent one. In correcting too great acidity, the *handlers,* or *rockers,* that first receive the green stock should receive the first treatment. Dilution with weak sweet liquor, or even with water, will help their condition. Sodium carbonate added to them will, of course, neutralize the acid, and soften the leather hardened by the excess of acid; but care must be taken as to the amount added, for too much sodium carbonate will make the stock too soft.

The addition of an antiseptic, as corrosive sublimate or carbolic acid, will stop the formation of acid, but will not lessen its amount. The former is the better antiseptic to use, as carbolic acid sometimes tends to darken and spot the leather. Since the antiseptics do not decrease the amount of actual acid present, they are best used in the yard vats to retard the development of acid in that quarter.

36. In a properly managed sole-leather yard, where bark liquors are used, deficiency or excess of acid is unusual. Some tanners pay no attention to this matter, depending on acids introduced into the first liquors for plumping. Commercial acetic and lactic acids are commonly used, and while they accomplish the end for which they are put in, they are unnecessary in a sole-leather yard, where natural means will generally furnish the acid required.

Where the commercial acids are used, continual vigilance must be exercised in paying attention to their strength and the amounts to be used; otherwise, the hides will not be uniformly plumped and the leather will show a corresponding non-uniformity of texture and fineness. With certain classes of hides used in making a special class of sole leather, sulphuric acid is used for plumping. The use of this agent will be discussed in the description of the manufacture of this leather.

37. The plumping is done in *handlers,* or *rockers,* which are vats containing liquors that have been weakened by usage and are well soured. The acids present effect the plumping, and the small quantity of tannin in the liquors serves partly to tan the exterior portions of the hides. To equalize the action of the liquors in these vats, the hides are handled, or rocked, so that all portions of the hide come in contact with the liquor, and the liquor itself is constantly in motion.

The handlers, or rockers, are generally arranged in sets of a number of vats varying in strength. In handling the hides, it was formerly the custom to lift each hide from the vat and throw it into the next vat in the set, this process continuing through all the vats in the set. It is customary now to tie the hides one to the other, and by means of a hand reel the continuous string of hides is moved from one vat to the other. The *hand reel* is a wooden-stripped cylinder mounted on a stand about 4 feet high and turned by means of a crank. In operation, the reel is placed between two vats, one man turning the crank while another starts the string of hides over the reel and then arranges them in the vat that receives them, the friction of the hides on the reel carrying them along.

Handling by rockers is done by means of a wooden frame hung by pivots in the center of the top of the vats, so as to give a dipping movement of 6 to 8 inches to each end of the frame. The hides are hung over sticks placed across the frame. Motion is imparted to the frames of the rockers by beams connected with overhead shafting. By this means all parts of the hide are kept in contact with the liquor which is well agitated. This end is also attained in some tanneries by hanging the hides in the vats and agitating the liquor by means of an air pump, which supplies air to the bottom of the vat. The air bubbling up through the liquor keeps it in motion.

SOLE-LEATHER MANUFACTURE

38. Methods of Tanning.—The simplest and most typical methods of tanning are those used in making sole leather. The tanning of other bark-tanned leathers is accomplished mainly by variations of these methods. For this reason, a discussion of the various processes of tanning in the manufacture of sole leather will precede the description of processes for the tanning of the skins used in the production of more delicate leathers.

The system at present pursued in the tannage of sole leather is the result of an evolutionary process depending on the selective ability of the tanners themselves. Few scientific discoveries have helped them, and the basic principles of their art have only recently received attention. This state of things is due to several causes: In the first place, in an art that has attained a high degree of perfection through the endeavors of generations of practical workers, we are apt to rest with the results achieved without questioning the principles involved. In the second place, the raw materials, hide and tannin, being organic bodies of an unknown, or at least of a very complex, nature, there was limited foundation for theories of their natural interactions until more knowledge of them was obtained. The field for applied research is very promising, however, and much has been done

in recent years to place this branch of the industry on a scientific basis.

39. Sole leather is always sold by weight, and the cost of the hide is from 50 to 70 per cent. of that of the finished product. The object of the tanner is to make as many pounds of leather from a given weight of hides as he can possibly produce. His degree of success in this is technically known as *gain*. In the case of green-salted hides, a large percentage of the hide, as it is bought, consists of water and salt and such impurities as dirt, dung, and blood, so that 100 pounds of green-salted hides will only make from 60 to 80 pounds of finished leather. The gain would be spoken of as a gain of from 60 to 80. Dry hides contain practically nothing but dried hide substance, and 100 pounds of this class of hides will make from 150 to 185 pounds of leather, the gain in this case being a gain of from 50 to 85.

With green hides, the gain is the amount of leather made from 100 pounds of hides; with dry hides, the gain is the amount of leather made from 100 pounds of hides, less 100.

40. Vegetable tannage is to a certain extent, no doubt, a chemical process, but after the final chemical reaction between the hide and the tannin has taken place, the product is capable of a further absorption of tannin; the point at which chemical reaction ends and physical absorption begins, has not been determined. Suffice it to say, that sole leather may contain from 20 to 50 per cent. of tannin, and yet in all cases it may be thoroughly cured and perfectly tanned. There is, however, a minimum limit at which hide treated with tannin is leather, and this limit is the satisfaction of the purely chemical affinity of the hide for tannin.

The whole process is an economical one; the tannin does not change materially while in solution, and it is almost completely recovered from the tan liquors by the hide during the process of tanning. With vegetable tannage, labor costs are low, the only disadvantage being the time consumed and consequent loss of interest on the money invested in the process.

41. There are three general varieties of sole leather made in the United States, the names given them indicating the bark used in tanning. They are *oak, hemlock,* and a combination of both, known as *union.* Each of these classes of leather has special modifications represented by special grades of leather. The greater part of the sole leather made in the United States is tanned by hemlock bark. European prejudice against this leather has been removed and immense quantities are annually exported. Hemlock leather is produced by two methods of tanning—*acid* and *non-acid.* Some *slaughter hemlock* is also made, but this forms only a small percentage of the output.

42. Oak Leather.—Leather made from hides tanned with oak bark is distinguished by its color and texture. Oak bark gives a deposit, or *bloom,* of ellagic-tannic acid on the leather, and oak leather is known as *scoured* or *Texas,* depending on the removal of this bloom.

The hides used are green and generally of native slaughter. The Texas hides are usually from range cattle, and are made mostly into unscoured leather; those hides which are not branded or have only small brands are used for scoured leather. South American hides make a good grained scoured leather and are in demand for men's shoes of the highest grade.

The hides are placed in the soaks for about 3 days, but the time may be shortened by using warm water and a loss in hide substance saved thereby. The water in the soaks is changed with each pack of hides. Some tanners remove the hides after the first day's soaking and replace the dirty water with fresh.

The hides may be fleshed after soaking or they may be put in the limes and the fleshing and unhairing done after they leave the limes. Different tanners have different methods of liming this class of hides. Some leave them in the limes as long as 5 days, while others complete the liming in 2 days, handling the hides continually and using a lime-sulphide mixture. It is claimed that a warm bath of, say, 100° to 110° F. given to the hides the night previous to unhairing, is beneficial.

After soaking, the hides may be split along the spine line into two sides, or the splitting may not occur until after liming, and in some tanneries the whole hide is tanned.

After unhairing and fleshing, it is the custom in some tanneries to bate the stock. With the amount of acid usually present in an oak tannery, however, this is unnecessary and is the exception rather than the rule. The hides are usually placed in a vat of clear water and permitted to remain there overnight. The hides are then suspended in the *rockers*, and the real tanning begins.

43. The rocker vats are in complete sections, piped so that liquor from the bottom of one vat is delivered to the top of the next. As liquor is supplied to the head, or strongest, rocker vat, it gradually works around through all the vats, being weakened in each by the presence of the hides, until it reaches the weakest, or tail-rocker, vat, from which it flows to waste. The stock is hung in this tail-rocker vat, and is here constantly rocked in contact with the liquor coming from the next vat, which gradually becomes stronger until it is receiving the strongest liquor and has become the head-rocker; the stock is then removed and is ready for the lay-away vats.

The object to be attained with the rocker liquors is the removal of the lime remaining in the grain (it being neutralized by the organic acids in the liquor), the swelling of the hide, and the setting of the color. The quality of the leather is determined by the work done in the rockers and handlers, according as the plumping, coloring, etc., is properly done.

The liquor used in the rockers should be old, mellow, and not strong. The strength of the liquor is regulated by the number of pits in use, so that the green hides should have sufficient acid to purge them of lime and properly start the plumping.

44. From the rockers the hides are taken to the main tanning yard, where the lay-away vats are located. These vats are generally 9 feet long, 7 feet wide, and 5½ feet deep. In these, the hides are laid out flat, one by one, and a thin layer of ground oak bark sprinkled over each hide. This bark should not be ground too fine, or the weight of the pack will

cause the hides to settle together too much and the circulation of the liquor will be prevented, thereby destroying one of the purposes of the bark, and ultimately resulting in imperfectly tanned leather. Each layer is treated in the same way, fresh tan or bark being used in each case.

After laying away has begun, the tanning is conducted on lines peculiar to the individual tanner. Each man has his own ideas as to how much liquor the hide should receive and under what conditions. In general, the hides are allowed to remain in a lay-away until the liquor in that vat is sapped. The hides are then removed, the liquor run off, and stronger liquor used after repacking the hides, as before.

TABLE I

LAYER SCHEDULE FOR OAK-BARK TANNING

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Approximate Percentage of Tannin
First	8	34	4.00
Second	12	38	4.25
Third	16	38	4.25
Fourth	25	40	4.75
Fifth	32	48	5.75

Each pack of hides is laid away from four to seven times, according to the theories and judgment of different tanners, the whole operation of laying away extending over a period of from 3 to 5 months. These successive lay-aways are called *layers* and are known as first, second, third, etc., layers, according as they represent the first, second, or third lay-away that the hides have received.

45. Tanners differ not only as to the number of layers that oak leather should receive, but also regarding the temperature and strength of the liquor on these layers. For example, the schedule shown in Table I is in effect in a large tannery where oak-bark tanning is employed.

46. In another successful tannery where the oak-bark tanning process is used, six and sometimes seven layers are given. The temperatures of the various layers are also kept well up, and if it is necessary to tan the hides in a shorter period, these increased temperatures, with proper regard for the strength of the liquors, will produce the desired effect. Only a few years have elapsed since the use of warm liquors in the yard was inaugurated, and they have not been well received by all tanners. The schedule followed in this yard is given in Table II.

TABLE II

LAYER SCHEDULE FOR OAK-BARK TANNING WITH WARM LIQUORS

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Temperature Degrees Fahrenheit	Approximate Percentage of Tannin
First	8	34	70	4.35
Second	11	38	75	5.00
Third	16	35	80	4.60
Fourth	25	40	90	5.15
Fifth	34	44	100	5.80
Sixth	48	50	110	6.40

The time taken for tanning by this schedule is a little longer than by the first one given, but the leather seems to be of a closer texture, better filled, and of better wear-resisting qualities.

The first-layer liquor in this yard is an old liquor—the sapped fifth layer—and the second-layer liquor is also an old liquor—the sapped sixth layer. The other liquors are new, sweet liquors made by strengthening oak-bark liquors with chestnut-wood extract.

47. Oiling and Drying the Leathers.—When the tanning is complete, the sides are taken from the last layer and thrown into warm water to clean the grain of sediment

or fine particles of bark. After rinsing, the sides are piled to drain overnight. They are then swabbed with cod oil, or a mixture of cod and other fish oils, or a mixture of mineral oil and fish oils. The swab used is a piece of sheepskin tanned with the wool on. The sides are then hung on sticks or by brass catches in the drying loft.

48. The drying loft is generally located over the vat yard; steam pipes are spread over the loft floor and rest on blocks that support the pipes and allow air to circulate around them. A slat-work floor over the pipes serves as the floor of the loft. Tight windows and ventilators are provided so that the proper adjustment of light and ventilation can be maintained. In some tanneries, the heat and ventilation are supplied by mechanical means, blowers carrying air to the loft and keeping the atmosphere in constant circulation. Without proper circulation the air becomes stagnant among the closely hung leather and the damp leather will become moldy. To aid in keeping the air in circulation, openings that may be regulated as to size are generally distributed around the floor of the loft. The same end may also be attained by forcing air into the loft at a pressure slightly above that of the atmosphere, thus effectually moving any stagnant air.

The leather is hung over poles whose ends rest on beams, or it may be held by an ingenious brass device in which the weight of the side causes friction to uphold it.

49. Rolling the Leather.—When thoroughly dry, the sides are taken from the drying loft to the rolling room and there brushed with water and made into covered piles. When properly tempered, the sides are oiled on the grain side, rolled and dried in the loft, and, when dry, are sorted for the market. The rolling of the leather serves to smooth the grain side and compress the leather, thus making it firmer. It also puts somewhat of a polish on the finished leather. Rolling is effected by machinery.

50. The **leather roller** is a machine consisting of a heavy beam having on its end a polished brass wheel. This

wheel is about 8 inches in diameter and has a 6-inch face. A crank gives to the beam a direct motion, allowing the brass wheel to move about 1 foot each way right and left. The leather is held under the moving wheel, or roller, on a small bed of brass conforming to the arc described by the roller. A foot-lever serves to raise this bed and makes the pressure of the moving roller light or heavy, according to the will of the operator. By moving the leather around under the roller, all parts of it are finally smoothed and polished.

51. In some tanneries, the vat sizes of which necessitate it, the hides are split into sides as they come out of the soaks or out of the limes. Whole-hide tannage is more economical as to labor costs in the yard, but side tannage is more economical in beam-house work.

A large, light-colored, and even deposit of bloom on oak leather is considered a mark of fine tannage; for some purposes, the leather is sold with the bloom removed and is then known as *scoured leather.* For this leather, the hides are split and rinsed as usual. Then they are scoured by the scouring machine, drained, oiled, and dried. After this, they are dipped in water, rolled, and dried, and then receive a final rolling before going to the sorting room.

52. Most of the old-style oak sole leather is made from hides tanned in the manner just mentioned; but a considerable amount of so-called oak leather is also sold that is tanned with oak bark and chestnut-wood extract by methods similar to those used for tanning non-acid hemlock and union crop leather. The leather is bleached, and it is oiled in the wheel instead of by hand; and, except in the matter of tanning materials used, the process of tanning is quite different from true oak tanning.

53. Non-Acid Hemlock Tanning.—In the non-acid hemlock process of tanning, the hides are swelled, or plumped, by the natural ferment acids in the tan liquors, while in the acid process, a solution of sulphuric acid is used to effect the plumping.

54. Treatment of the Hides.—With the non-acid hemlock process, the hides used are generally dried South- or Central-American skins. They are well soaked and softened with the help of the hide mill. It is the usual practice to soak the hides from 5 to 8 days; then they are milled and thrown back into water for another shorter period. They are then milled again and may receive another day's soaking before the tanner considers them soft enough for good results. After soaking, they are split along the spine line into sides, and the hair is removed by either sweating or liming. After the removal of the hair and fleshing, the sides are soaked overnight in water and are then ready for the handlers. Limed stock is bated in some tanneries, a light bran or hen-manure bate being used. Before putting it in the handlers, some tanners *color* the stock by running it for a few minutes in a paddle wheel revolving in a vat of acid spent liquor of from 8° to 12° Bk.

55. The sides are strung together for handling by tying a shank of one to the shank of the next, and the string of hides is then dropped into the tail, or weakest, handler vat. The handler vats are arranged in continuous sections that are so connected that liquor run into the head vat passes successively through the other vats in the section, flowing from the top of one vat to the bottom of the next. Hand or power reels are placed between each pair of vats so that the string of sides may be easily moved from one vat to the other. The handler liquors are sapped liquor, generally from the first three layers of the lay-away yard; they are weak in tannin and contain the natural plumping acids. The head, or strongest, handler liquors are generally from 14° to 18° Bk., and are sapped by the green stock until the tail, or weakest, handler liquor becomes of a gravity not much above 8° Bk. The strength of the handler liquors depends on the strength of the lay-away yard, which is controlled by the method of the tanner in charge. The stock is put into the tail-handlers and reeled forwards and backwards, perhaps every hour during the first 24 hours, and possibly eight or ten times during the sec-

ond day. This reeling serves to change the position of the stock as it lies in the liquor, plunges the liquor, brings every part of the hide in contact with the liquor, and equalizes the effect of the tannin and color on the green stock. After the first 2 or 3 days in the handler liquor, the stock is reeled forwards once every day into a stronger vat until the head-handler or strongest handler is reached; and, the handler liquors having accomplished the plumping and started the tanning, the strings are removed and the stock goes to the lay-away yard. Here, the stock receives from five to seven layers in liquors of different strength, according to the methods in use at the tannery.

56. A schedule in use at a successful non-acid tannery is given in Table III.

TABLE III

LAYER SCHEDULE FOR NON-ACID TANNING

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Approximate Percentage of Tannin
First	7	21	2.85
Second	11	22	3.40
Third	12	23	3.60
Fourth	18	24	3.75
Fifth	19	28	4.00
Sixth	26	28	4.00

In this tannery the liquors are used at a temperature of from 70° to 75° F. on all the layers. The first layer is an old liquor that has been sapped by usage on the fifth layer, and the second-layer liquor is also old, having been sapped on the sixth layer. The third-, fourth-, fifth-, and sixth-layer liquors are all sweet liquors made by strengthening leach-house liquor with extract. The sapped liquors from the first, second, and third layers are used as handler liquors; the fourth layer

sapped is returned to the leach house, and the fifth and sixth layers sapped, as just explained, are used for first- and second-layer new liquors, respectively.

The hides are kept in the first-layer liquor for the required number of days. The pack is then hoisted, the old liquor removed for handler purposes, and the hides placed in the second layer. This process of treating the skins to successively stronger tanning liquors goes on until the last layer is reached. The leather is then finished so far as actual tanning is concerned. The length of time for each layer is a matter determined by the judgment of the tanner, and therefore differs with conditions. Theoretically, it would be best to allow a pack of hides to remain in a layer until there was no more sappage, or taking up, of tannin by the hides. After the tannin contents of hide and liquor are equal, months of further contact will not put any more tannin in the hide in that layer.

TABLE IV

LAYER SCHEDULE FOR NON-ACID TANNING WITH WARM LIQUORS

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Temperature Degrees Fahrenheit	Approximate Percentage of Tannin
First	5	28	70	3.15
Second	12	30	80	3.40
Third	14	32	85	3.60
Fourth	18	34	90	4.00
Fifth	20	38	100	4.75
Sixth	24	40	110	5.00

57. Use of Warm Liquors.—There is some prejudice against the use of warm liquors in a tan yard, but if the proper limit of heat is not passed, the results seem to be beneficial. By the use of warm liquors, the length of time on the first layers is shortened and stronger liquors used. In one tannery where warm liquors are used, six layers of liquor are given

to the stock. The schedule of this tannery is shown in Table IV.

The liquors at this tannery are made up as follows: The first-layer new liquor is the sapped liquor from the fifth layer; the second-layer new liquor is made by taking equal portions of the sixth-layer sapped liquor and liquor from the leach house. The third-, fourth-, fifth-, and sixth-layer new liquors are made by strengthening leach-house liquors with chestnut-wood extract.

The temperatures on the different layers are adhered to within a range of 5 degrees either way. With these warm liquors, the duration of the tanning process may be shortened, but an increased period does not harm the stock.

With the old process of tanning, the leather, after coming out of the last layer, is thrown into a pool of water to remove the sediment that has accumulated on the surface of the leather. This is also frequently accomplished by placing the leather in a drum with water and revolving it for a few minutes.

58. Bleaching.—After the rinsing process, the leather is piled to drain and then bleached. The bleaching to which sole leather is usually subjected is not really a bleaching process, because the excess of tannin on the surface of the leather, which lightens the color of the stock and also makes it less liable to crack, is simply dissolved and removed. The bleaching consists in dipping the leather into an alkaline bath that dissolves and removes the excess tannin, then into an acid bath that neutralizes any soda remaining on the leather, and finally into water to remove the remaining acid. For convenience in handling the leather, the three vats are placed in a row, and the leather, hung on sticks supported on a frame, goes into one vat for the desired time. Then, the frame is raised and the leather drained, after which it is put into the next vat. This process is continued until the bleaching is completed. The time necessary for the reaction that takes places in each bath is utilized by the workman in unloading a frame of bleached leather and in loading a frame of leather ready to be bleached.

Sodium carbonate, as sal soda or as soda ash, is the alkali generally used, because it is the cheapest; and, for the same reason, sulphuric acid is the acid always used. The tanner regulates the strength of the bleach by varying the quantity of soda ash or sal soda (and accordingly the acid), the strength depending on the color desired.

59. After bleaching, the leather is hung or piled to drain and to dry off slightly before oiling. Hand oiling is now rarely employed, the majority of tanners applying the oil in the oil wheel. The oil wheel is simply a revolving wooden drum fitted with a removable door, and hollow axles through which the oil is pumped. The oil used is either cod oil, winter-pressed fish oil, or mineral oil, or mixtures of these oils. Many tanners adhere to the use of cod oil, but a good grade of fish oil from which the sediment has been removed by pressing while chilled—or what is known as winter-pressed oil—will give the same results as cod oil and is cheaper. The mineral oil is cheaper than either fish or cod oil and gives satisfactory results when mixed with higher-priced oils.

60. The color of sole leather is one factor that determines its market price, and although it seems the height of folly to demand a qualification that does not affect the quality of a product, yet the extent to which this demand for a good color has been carried has resulted in recourse to means of supplying the demand. In the hands of some tanners, these means have been used for the accomplishment of an end other than the one originally intended, and as a result, there is considerable cry about the adulteration of American sole leather. Leather dried in the rough, unless so heavily bleached as to remove too much of its weight, is liable to become dark at certain points on the side. The addition of a small amount of a mixture of glucose, or grape sugar, and sulphate of either magnesium or sodium, to the leather, serves to overcome this tendency and results in a leather that dries easily and finishes bright. In addition to these benefits, the leather thus treated will have firmer flanks and bellies, and it remains in better physical condition, so that it can be cut and worked more readily. The

amounts of the materials necessary to produce these results in a side of leather are so small that their use for this purpose cannot be called an adulteration. The ease with which these materials can be added, however, has, of course, resulted in the production of some cheap, adulterated leather.

61. The glucose and salts are generally added with the oil in the oil wheel. When the leather is in the proper condition for oiling, it is thrown into the oil wheel and ¼ pound of Epsom or Glauber salts and ½ pound of glucose for each side, are also thrown in. The door is then put on and clamped, the oil pumped in through the hollow axle, and the wheel revolved from 30 to 60 minutes. At the end of this time, the revolving wheel has caused the tumbling leather it contains to absorb oil and other materials added, and the leather is removed on trucks to the dry loft, where it is hung on sticks and dried.

For the first day or so after lofting the leather, drying progresses without steam or light, but with proper ventilation. The temperature of the loft is then gradually raised until the drying is complete. This process requires from 10 to 25 days, depending on weather and local loft conditions.

After the leather is thoroughly dried, it is taken down, dipped into warm water, and piled down to *sammie*, or to equalize, for 1 to 2 days. Warm water is then sprinkled on the grain side, care being taken that every portion is wet. Then the leather is swabbed with cod or other fish oil, after which it goes to the rollers for a first rolling. After the first rolling, the leather may be hung and thoroughly dried before the second rolling, or it may be piled and second-rolled while in a comparatively wet condition. After second rolling, the leather is hung by one end in the finished-leather loft and, when dry, is sorted and graded for market.

62. Wheeling or Extracting.—In most of the tanneries of the present, the time of tanning in the yard has been materially shortened and the weight that the hide does not receive in the yard is given it by *wheeling* with the tanning solutions. The wheels used for this purpose are from 8 to 10 feet in

diameter and from 5 to 6 feet wide; they are mounted on trunnions and revolved on a horizontal axis by a pinion geared to teeth set around the perimeter of the wheel. A removable tight door secured by clamps provides for the loading and unloading of the wheel, and tannin solution is pumped into the wheel through its hollow axle.

The methods of wheeling and methods of actual tanning vary to the same extent. Each tanner has his own ideas as to the treatment of the stock before and after wheeling, as to the amount, temperature, character, and strength of the tanning solution, and as to the duration of the wheeling. The character, size, and the condition of the leather all determine the kind of treatment to be used, and the tanner's experience tells him what treatment will produce the best results under given conditions.

63. After the yard tanning is complete, the leather is thrown into water to wash off any adhering sediment, and it is then hooked out and goes to the *wringer,* which is a mammoth clothes wringer provided with felt-covered brass rolls. The leather is fed into the wringer and comes out with the excess of moisture removed. As the sides of stock come from the wringer, they are piled on trucks, taken to the wheels, and thrown in. The door is put on, clamped in place, and the wheeling materials pumped into the wheel. The materials used include all kinds of tanning liquors, such as chestnut wood, oak bark, hemlock bark, quebracho, sumac, quercitron, and other liquors, varying in strength from 100° Bk. to the undiluted extract running from 42° to 50° Twaddell (210° to 250° Bk.). The temperature at which these materials are used varies from 100° to 160° F., according to the practice of the tanner. After the leather and wheeling material have been put into the wheel, the power is applied and the wheel makes from 15 to 20 revolutions per minute, the speed varying according to the diameter. The revolution causes the leather to roll and fall within the wheel, and, being in constant contact with the tanning solution, the latter is mechanically absorbed and incorporated into the leather.

64. The completeness with which the wheeling material is absorbed depends on the character, size, and condition of the stock, and obviously on the amount of solution added to the wheel. The amount varies from a quantity of solution that represents 1 pound of solids to the side to a quantity representing 4 pounds to the side. The duration of the wheeling varies from 45 minutes to 2 hours, and on the expiration of the required time, the wheel is stopped, the door removed, and the contents of the wheel removed to a truck. From the wheel, the stock may be piled in low, covered piles, it may be hung over sticks in a dark, cool place, or it may be laid away in strong-liquor vats. This treatment is for the purpose of allowing the mechanically added material to permeate the leather thoroughly and uniformly. After piling, hanging, or laying away the stock for the desired period, it is taken to the bleach room. From this point until the leather is finished, the operations are the same as for leather that has not been wheeled.

65. Acid Hemlock Leather.—By acid hemlock leather is meant a variety of hemlock sole leather that has been plumped by means of sulphuric acid. Other kinds of sole leather are made from hides that are plumped by organic acids, which are either naturally present in the liquors or have been added to them. The sulphuric acid causes an abnormal distension of the pores and swelling of the tissues.

Most of the acid hemlock leather is made from dried hides; that which is made from green hides is known as *slaughter hemlock sole*. The process of manufacture is the same, except that the hides, being green, are generally depilated by means of lime instead of by sweating. The dried hides are largely of South American or of Asiatic origin, this being a very popular method of tanning the Chinese *Buffalo* hides.

The hides are soaked, limed or sweated, depilated, and fleshed in the usual manner and then soaked in clear water. After this they go into a weak tanning liquor. This liquor exerts its slightly astringent effect on the hides, and they are somewhat colored by the bath.

66. Plumping With Sulphuric Acid.—After the treatment just mentioned, the hides are put into a .1 to .3 per cent. solution of sulphuric acid and kept there until the swelling has progressed to the desired stage. They are then ready for the tan yard.

Because of the abnormal plumping by the sulphuric acid, the hides can safely be put into strong liquors. In the other processes of sole-leather tanning, the hides receive weak-liquor treatment, the strength being gradually raised until the maximum is attained. In this branch of the industry, there are no true rockers, or handlers. The only tannin treatment they receive before going to the first-layer liquor is the slight coloring from the weak tanning solution before plumping.

After plumping, the hides go to the first-layer liquors for the time required for this layer. The first-layer liquor in an acid tannery soon becomes impregnated with sulphuric acid and sulphates, and must then be discarded. The free sulphuric-acid content is generally not very high in this liquor, but there is sufficient to interfere with the tanning action. The liquors become very dense and the proportion of tannin to the total solids is low, so that there is little sappage to be obtained. The gravity of this first-layer sapped, or *run-to-creek*, liquor is from 18° to 25° Bk. and it will contain from .8 to 1.5 per cent. of tannin.

A great deal of thought has been spent in trying to devise some method of saving the tannin and to avoid the necessity of running this strong filth-bearing liquor into, and thus contaminating, a stream. The removal of the sulphates by precipitation with barium chloride and subsequent settling has also been proposed. In some tanneries, the practice is to run this liquor over a spent leach of tan bark; this process removes the free acid as well as some of the solid impurities.

67. As in the case of the other sole-leather tanning processes, there are various systems in use in this branch of the industry. There is a little more latitude here, however, than in oak or non-acid hemlock tanning, the first-layer liquor being used in many strengths by different tanners. The liquors

are made by combining bark and extract liquors according to the latest practice of all sole-leather tanners; from five to seven layers of liquors are used, either cold or warm. A schedule of strengths in a cold-liquor tannery is given in Table V.

The first-layer liquor is a sixth-layer liquor that has been sapped by a tanned pack. All the other liquors are made from leach-house liquor or leach-house liquor strengthened

TABLE V

LAYER SCHEDULE FOR ACID HEMLOCK TANNING WITH COLD LIQUOR

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Approximate Percentage of Tannin
First	8	38	3.60
Second	11	40	3.90
Third	15	42	4.20
Fourth	24	42	4.50
Fifth	24	44	5.00
Sixth	27	48	5.40

with chestnut-wood extract. The sapped first-layer liquor is run to waste, and the other sapped liquors (with the exception of the sixth layer) are returned to the leach house.

68. In Table VI is given the schedule followed in a warm-liquor tannery using seven layers of liquors.

In this tannery, the first-layer liquor is a sixth-layer liquor that has been sapped, the second layer is a seventh-layer liquor that has been sapped, while the other liquors are leach-house liquors made by building up all sap liquors but the first and seventh, which are run to waste and to first-layer new, respectively.

After the leather has been tanned in the yard, it is further treated by the methods described under the head of Non-Acid Hemlock Tanning.

69. Acid slaughter sole leather is made from green hides, the hair being removed by either liming or sweating. When the hides are limed, a bate is sometimes used in the production of this variety of leather, but otherwise the liquors and operations are the same as in the manufacture of the regular acid hemlock leather. The use of sulphuric acid as a plumping agent results in the production of a firmer leather. The action of the acid is much more energetic on sweated hides than on limed stock, because in the limed-stock treatment, part of the acid is neutralized. Therefore, in the regular acid process, care must be observed as to the degree of plumpness attained.

TABLE VI

LAYER SCHEDULE FOR ACID HEMLOCK TANNING WITH WARM LIQUOR

Layer	Strength of Liquor Degrees Barkometer	Time in Layer Days	Temperature Degrees Fahrenheit	Approximate Percentage of Tannin
First	7	27	65	2.50
Second	9	29	75	2.80
Third	12	30	85	3.00
Fourth	13	32	90	3.20
Fifth	15	34	100	3.40
Sixth	19	34	105	3.80
Seventh ...	28	36	110	4.10

70. Union Leather.—The combination of hemlock and oak barks gives a very serviceable leather known as *union sole leather*, which has a better texture than hemlock-tanned leather, is tougher, and has a color somewhat like that of oak-tanned leather. There is probably more variation in the processes of making this leather than in making other kinds of sole leather.

Color is all-important, and many methods for its improvements are being used. Some go back to the leach house to aid color, and sacrifice tannin there in order to have very pure

liquors, which will give the leather a bright, clean shade. An illustration of the wide difference in union methods may be seen in the fact that in some union tanneries the first-layer liquors are as low as 8° Bk., while in others they run as high as 25° Bk. These liquors are, however, not of the same purity. The 8° liquor will show a higher proportion of tannin to the total solids than the 25° liquor, but, aside from this, the tannin strength of the 25° liquor is greater than that of 8° liquor. In tanneries where strong liquors are employed, considerable oak or chestnut-oak extract is used, the upper layers being strengthened, and the texture and color improved thereby.

71. Most of the union leather made is cropped; that is, the bellies and shanks are cut from the sides, making the product rectangular. The crop leather thus made commands a higher price than union side leather, because much waste is avoided when it is cut into soles. The bellies, shanks, etc. are sold for scrap leather for inner soling, etc. A good quality of cut soles is made from union leather, and the method of selling these cut soles determines the method of tannage in some tanneries. A certain number of soles will be cut from several tannages of leather, and the leather that will give the largest number of soles to a given weight of leather is generally the best seller, if other considerations, as color, firmness, and texture, are equal. This causes tanners to endeavor to produce a light crop leather of a good color, strength, and closeness of texture. These qualities can be obtained by the use of very pure liquors of low barkometer degree. Since purity of the liquor is secured at the expense of leaching, it is really questionable whether this method of tanning pays. More leather can be made from a ton of bark by this process, but the actual gains will not be so great as when a heavy, well-filled leather is produced.

72. Green-salted hides are used for making union leather. They are well soaked, limed, unhaired, fleshed, and placed in clear water overnight, after which the hides go into the rockers. According to the method of tanning in use, the

rocker liquor and all other liquors vary in strength. After coming from the rockers, the leather is cropped in some tanneries, while in others it is tanned and finished as side leather and then cropped. When cropped out of the rockers, the heads and bellies are strung together and thrown on top of the regular leather in the lay-away vats. From the rockers, the sides go into the lay-away yard; from five to seven layers are given, using oak bark on every layer. The oak bark is ground fine, but not fine enough to prevent the circulation of liquor between the sides in the vats. After use in the lay-aways, the bark is sent to the leach house and leached with the hemlock bark for the union liquors. It is generally placed on the bottom of a leach, the hemlock bark being run in on top of it.

TABLE VII

LAYER SCHEDULE FOR UNION TANNING WITH COLD LIQUOR

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Approximate Percentage of Tannin
First	6	14	2.25
Second	10	16	2.50
Third	10	18	2.75
Fourth	12	20	3.25
Fifth	15	23	3.75
Sixth	25	25	4.50

73. A schedule of layers and liquors in a tannery using cold, weak liquors is shown in Table VII.

The leather from this tannery is of a very beautiful color, light in weight, and quickly tanned. The sapped liquors are strengthened by returning to the leach house, and no extract is used. The liquors are very pure; in fact, some of them are of such purity that 65 per cent. of the total solids are tannins. With this purity, the spent tan, of course, shows considerable tannin, the amount sometimes running as high as 2.25 per cent. The sides are completely tanned here and are

cropped after finishing. The yard operations are carried on in the usual manner, and the sapped upper layers which return, to do duty as lower layers, are strengthened in the leach house.

74. To show the difference in methods, the schedule of another cold-liquor tannery is given in Table VIII.

This tannery is a typical, modern, union crop tannery, no oak bark, excepting that used for dusting between the leather in the lay-aways, being employed. The union color is made by combining hemlock-, quebracho-, and chestnut-wood liquors, the resulting leather having a good color and all the physical

TABLE VIII

LAYER SCHEDULE FOR UNION TANNING WITH COLD LIQUOR

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Approximate Percentage of Tannin
First	7	16	2.50
Second	11	21	3.25
Third	14	21	3.25
Fourth	22	23	3.75
Fifth	33	25	4.50

characteristics of union leather. The fifth-layer sapped liquor is used for the first-layer new liquor, the fourth-, third-, second-, and first-layer sapped liquors being used as rocker liquors. The new liquors (except first layer) are made by strengthening the leach-house liquor with equal portions of quebracho- and chestnut-wood extract.

75. A warm-liquor tannery using strong liquors and considerable extract had the schedule given in Table IX.

Six layers were in use at the tannery, although ordinarily but five are given. This tannery makes rather heavy leather, of a good color, and the bark used is well leached. Extract

is used for strengthening the liquors, some of which are returned to the leach house for strengthening.

76. The use of weak or strong yard liquors depends on the expected finishing treatment of the leather. In a tannery using wheels for the mechanical addition of tanning material to the leather, the yard liquors are generally weaker in barkometer strength and higher in purity than in yards pursuing the old methods of union-leather tanning. After the yard tanning, the leather is cropped, provided this operation has not been performed previously. It is then finished by rinsing, bleaching, oiling, drying, and rolling, as has been previously

TABLE IX

LAYER SCHEDULE FOR UNION TANNING WITH WARM LIQUOR

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Temperature Degrees Fahrenheit	Approximate Percentage of Tannin
First	7	22	65	3.00
Second	11	24	75	3.50
Third	14	26	80	4.00
Fourth	20	28	90	4.60
Fifth	25	31	100	5.00
Sixth	33	34	105	5.60

described; or, if preferred, it may be wheeled with tanning material, as described under the head of Non-Acid Hemlock Tanning, and then finished in the regular manner. Union crop leather is generally rolled only once, the gloss of hemlock leather not being required on union leather.

77. Quick Sole-Leather Tannage.—To tie up the immense amount of money that is represented by hides in process of tanning by ordinary methods of making sole leather, requires either a large working capital or excellent credit. In either case, the interest on this tied-up money is a considerable item in the cost of tanning. For this reason principally, quick-

tannage methods have been and are being devised with the hope of producing a leather as good as the long-tanned product and without the necessity of employing as much unproductive capital as the manufacture of the latter entails.

Many methods of quick tannage have been devised, some of them of proved merit. Others are useless, some of them being merely schemes of unscrupulous promoters. The most of the methods depend on the constant agitation of the hide in the presence of the tanning agent to produce the quickly tanned leather so much desired. It is in the preliminary treatment of the hides and in the strength and method of applying the tanning material that the methods differ. The claims as to time required vary with each process, some being as low as 48 hours from the time the hide leaves the beam house until it is said to be ready for the dry loft.

In one general class of these quick tannages, rockers similar to those used in the first stages of some kinds of the regular-process sole leather, are employed. In another, revolving wheels, or drums, are used for a part or all of the tanning process.

78. In the process involving rockers, the stock that comes from the beam house is hung on rockers in the tanning vats. The vats are in complete sections and are equipped with the press system. The top of one vat is connected with the bottom of the next, and the liquor supplied to the head, or strongest-liquor, vat gradually works around through all the vats to the weakest-liquor vat, from which it flows to waste, or else to be strengthened. The stock is hung in the vat receiving the weakest liquor, and here it is constantly rocked in contact with liquor coming from the next vat. The liquor gradually becomes stronger until the vat is receiving the strongest liquor. The stock is then removed and may be put into a strong lay-away vat for a few days, or it may be wheeled with strong liquor or extract, according to the particular quick-tannage process that is being used. In some processes, the hides receive a chemical treatment before going into the tan liquors. One method calls for rocking in a liquor composed of salt, alum,

and sodium nitrate; another calls for a light chrome treatment, while others call for other baths of single chemicals or combinations of chemicals. Treatment with weak organic acids is also generally resorted to, in order to bate and plump the stock before going into the tan liquor. All these chemical baths are designed to open the pores of the hide, so as to facilitate the quick combination of the tanning material with the hide, to prevent the *drawing*, or closing up, of the grain when the hide comes in contact with a strong tanning solution, and to taw the hide slightly, so that the absorption of vegetable tannin by the partly mineral-tanned hide is increased and quickened.

79. Another general class of quick-tanning processes requires the use of the revolving drum, or wheel, to effect the tanning. Various styles of wheels have been introduced and patented, and in many cases the style of wheel or drum used is the only protected feature of the process. The wheels are generally about 10 feet in diameter and are revolved at varying speeds. The interior of the wheels used in some processes are fitted with arrangements for fastening the hides by one end or edge, so that as the wheel revolves the hides are submerged in the tan liquor at one point of the revolution and stretched out and drained at another point. Another style of wheel has a removable frame shaped like a skeleton wheel, on which the hides are fastened in a parallel row, the frame being then fastened within the wheel, with which it revolves.

Another patented wheel contains a removable frame to which the hides are attached in a parallel row, but which does not revolve with the wheel. The frame is so constructed that the hides fastened to it are stretched in alternate directions by mechanism actuated by the turning of the wheel. The hide frame remaining stationary, the tan liquor is poured over the hides by means of buckets or carriers attached to the interior of the revolving wheel. The buckets scoop up the liquor at the low point of the revolution and dump it at the high point, thus allowing it to fall over the hides attached to the stationary frame.

All the wheels are fitted so as to allow the admission or removal of the tanning material without interfering with their revolution. One process employs a wheel in which the tanning material in the shape of solid extract is placed in latticed receptacles within the wheel, the weak liquor used in starting being strengthened by the slowly dissolving extract. The wheels used in processes requiring heat, or the admission of air or other gases, are arranged to meet all the requirements of the process.

80. In general, the treatment of the hides in quick-tannage processes using wheels is the same as in the processes using rockers. Some processes call for a preliminary treatment, and others begin with the hide just as received from the beam house. Weak liquors are first supplied to the wheels, the strength being gradually increased as the tanning progresses, until the maximum strength of liquor is being used and the wheel tanning is completed. The wheels are sometimes run in sets, the liquor from a wheel containing hides nearly tanned being run to the next wheel in which the tanning is not so far advanced, and so on to the wheel containing fresh hides. From here, the liquor is run either to waste or to storage to be strengthened. Where the wheel is operated as a unit, each sapped liquor may be run off to give place to a stronger one, or the liquor may be strengthened in the wheel by the addition of strong liquor or extract.

After the wheel treatment, the stock may be bleached and lofted, as in some processes, or it may receive a further treatment by laying away for a few days in a strong liquor, or by being thrown loose into revolving wheels containing strong liquor or extract. When the tanning is completed, the leather is bleached, oiled, dried, and rolled in the same manner as the regular long-tanned leather.

81. Most of the quick-tannage processes are still in the experimental stage, and they find many opponents among the old-style tanners. The principal objection to the processes themselves is found in the accumulation of weak tanning liquor. The hides are treated so that their affinity for

tannin is developed to the highest point, and the strong liquors they receive are sapped quickly; thus, a liquor containing a preponderance of non-tanning matters ultimately results. These sapped liquors may contain considerable tannin, but in the presence of such a large proportion of non-tannins, the tannin itself is not very active and is not available for quick-tanning purposes. The constant strengthening of these liquors serves only to postpone the ultimate end of their usefulness and to increase proportionately the barkometer strength of the waste liquors.

The principal objection to the manufacture of sole leather by quick processes has been its low gain. Unless loaded, or weighted with adulterants, the quick-tanned leather produced at a cost allowing a profit to the tanner, does not show the gain that it is possible to make by the older methods of tanning. In the beginning of the quick process, the first leather produced may show up well as to gain and as to cost of manufacture, but as the process continues it has been the experience of many that gain decreases and costs increase. The waste of unavailable tannin in the sapped liquors and the decreasing purity of the tan liquors are responsible for this condition.

There is also an objection to quick-tanned sole leather simply because it is quick tanned, some persons claiming that it is impossible by shorter processes, to produce a leather with the toughness, mellowness, and fiber of the long-tanned methods. This cannot be proved by the characteristics of quick-tanned leathers taken as a class, as leather produced by quick-tannage methods varies in appearance, texture, and strength just as much as the long-tanned leather.

As previously stated, most of the quick-tanning processes are still in the experimental stage, and the exact status of quick-tanned leather is not yet determined. From present indications, however, it would seem that in the near future the practicability and economy of the quick tanning of sole leather will be demonstrated. Whether experience will show it to be the equal of the old-style leather remains to be seen.

MANUFACTURE OF LEATHER
(PART 2)

HEAVY, OR FIRM, LEATHER—(Continued)

SOLE-LEATHER MANUFACTURE—(Continued)

OAK-TANNED BELTING LEATHER

1. Oak-tanned belting leather is really a sole leather, slight changes in the tanning and in the treatment of the leather after tanning being made to produce the tough, mellow leather that is required for belts. The hides should be the best, and the unbranded packer steer hide is used largely for this purpose. The beam-house process is about the same as for other oak leather, except that the hide is not split into sides. The hides are thrown over sticks and hung in the handler liquors, instead of being strung together. After coming out of the handlers, the bellies are trimmed off, and sometimes the heads are taken off at this point. The parts trimmed off are strung together and tanned separately, or they may be thrown in on top of the regular stock.

After trimming out the handlers, the hides, or *butts*, are laid on frames in the lay-away vats and care used to spread out smoothly and remove all creases. The frames are held by ropes attached to the corners and are gradually lowered into the vat as the height of the hides on the frame increases. This stock is generally given five or six layers, the first, and sometimes the second, being sour liquors that have been sapped by higher layers.

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

2. The schedule for a typical belting butt yard is given in Table I.

The leather is hoisted twice while in the first lay-away liquor, the hides being removed and carefully piled beside the vat. The creases and folds are removed and the hides flattened out in the piling, and the leather is again laid away in the same liquor. This treatment seems to improve the quality of the butts, and while it is not followed in all tanneries, the appearance of the finished product that has undergone this treatment in the yard would indicate that it is worth while. If the leather out of the first layer is flat and free from creases,

TABLE I

LAYER SCHEDULE FOR OAK-TANNED BELTING LEATHER

Layer	Character	Strength Degrees Barkometer*	Time in Days
First.....	Sour	37	15
Second.....	Sweet	30	10
Third.....	Sweet	33	15
Fourth.....	Sweet	38	30
Fifth.....	Sweet	50	50

there is small probability that the higher layers will cause a permanent crease or wrinkle, as the first layer tends to firm up the soft stock from the handlers.

After being raised from the last layer, the stock is put into cold water overnight, and then into water ranging from 90° to 100° F. for the same length of time. It is then taken out of the warm water, carefully piled, and allowed to drain. When drained, it receives a hand oiling with cod oil on the flesh side and it is again piled to allow the oil to work into the leather. The leather is then lightly oiled on the grain side, taken to the dry loft, and, when dry, is ready for shipment.

*See Art. 23.

3. Harness Leather.—Green, salted, heavy cow and steer hides that go through the regular liming process in the beam house are used for harness leather. The hides are bated with oropon, or with an organic-acid solution. Rockers are used to rock the sides in the first weak tanning liquors. After the rocker treatment they receive three or four lay-away liquors, oak bark being used between the layers of leather in the vats. The best harness leather is pure oak-bark tanned, but much of the present product is tanned with liquors made up of chestnut-wood and quebracho extract in combination with oak- and hemlock-bark liquors. The flesh is given a smooth surface by *skiving*, or shaving, when the leather is pretty well struck through.

4. After tanning the leather is scoured. It then receives a light coat of cod oil on the grain side and is hung up to sammie, or season. When properly seasoned, the sides are thrown on the setting table, the flesh smeared with tallow and oil, and the grain side thoroughly worked with a stone. It is then given another coat of cod oil. The flesh side is then worked, additional oil and tallow are put on, and the side suspended to dry slowly. When nearly dry, the grain side is again worked, or set, and oiled, and the side is again hung up to dry. From the loft the leather is piled and remains in the piles for 10 days or more, when it is buffed and blacked. The buffing is generally done by hand, a light shaving of the grain being removed to obtain a uniformly smooth surface. After buffing a hot solution of sal soda and logwood is applied with a stiff-bristled brush, and thoroughly rubbed in. This saponifies the surface grease and oil, so that it will not interfere with the coloring. It also mellows the grain of the leather. The blacking is then applied with a soft brush, or swab, and then allowed to dry partly. After this another application of a thin mixture of oil and tallow or stearin is given the leather, which is rehung on sticks. After a hand setting-out on the following day, a final coating of oil and tallow is applied and the leather is again hung up to dry. After drying the sides are removed from the racks and arranged in piles where they remain from 1 to 2

weeks. The leather from the piles is finished by slicking off the grease from the flesh side and smoothing it. The grain side is then slicked and brushed and finally rubbed with a woolen cloth. The leather is then trimmed and graded for market.

VEGETABLE TANNING MATERIALS

5. As a result of the diligent research that has been going on for many years the number of available vegetable tannins has been greatly increased and as a result the cost of tanning materials has been lessened.

Of late years the economical leaching of the bark has served to lengthen the time during which the native barks will be available. The use of wood extracts has also served to protect and increase the life of bark tanning, and as the supply of wood from which these extracts are made is practically unlimited, this generation at least has nothing to fear from a shortage of tannins.

6. In tanning hides for sole leather, the following vegetable tanning materials are most frequently used:

Hemlock bark is the most important vegetable tanning material used in America, about 60 per cent. of all leather being tanned by it. It is the bark of *Abies Canadensis*, and in the East it contains about 11 per cent. of tannin. The tannin content of Western hemlock runs as high as 18 per cent. Hides tanned with it make tougher leather than those tanned with oak bark, but the leather is not as pliable. Both solid and liquid extracts of hemlock bark are also on the market.

Oak bark is also one of the important tanning materials. It is the inner bark of several varieties of the oak tree, as the English oak (*Quercus robur*), the rock-chestnut oak (*Quercus monticola*), and the yellow oak (*Quercus tinctoria*). White oak (*Quercus alba*) and the red oak (*Quercus rubra*) are not so valuable because of their lower tannin content and undesirable color. The tannin of the several varieties of oak is known as quercitannic acid, $C_{17}H_6O_9$. There are four anhydrides of this acid, the first, phlobaphene, $C_{34}H_{30}O_{17}$; the second, $C_{34}H_{28}O_{16}$;

the third, Oser's oak red, $C_{34}H_{26}O_{15}$; and the fourth, Löwe's oak red, $C_{34}H_{24}O_{14}$. Quercitannic acid and phlobaphene only are of importance in tanning.

Canaigre (*Rumex hymenosepalus*) is a native of the dry Southwest. Some recent attempts have been made to cultivate it and introduce it as a tanning material, but with little success. The coloring matters and starch extracted from it affect the quality of the leather.

Quebracho is the name of several hardwood trees growing in South America. The wood and bark of *Quebracho colorado* contain from 15 to 20 per cent. of a bright-red tannin, but do not contain enough non-tannins to aid the formation of fermentative acids necessary to plumping, nor will it yield a full, well-nourished leather unless combined with other forms of tanning agents that are richer in non-tannins.

Palmetto root is obtained from the palmetto tree found abundantly in the Southern lowlands. This root has been attracting considerable attention for the past few years among Southern tanneries. The root is cut up and treated like bark. Its action is quick, and the leather tanned by it is tough.

Gambier (*pale catechu*) is an important tanning agent. It is the dried extract from the leaves of *Uncaria gambier* and *Uncaria acida*. The extract is readily soluble in warm water. It contains from 36 to 40 per cent. of a brown tannin that penetrates hides rapidly and tends to swell them; taken alone, it produces a soft, porous tannage. It is largely used with other tanning materials for both light and heavy leathers. It is exported from Singapore in pressed blocks and cubes.

Catechu, or *cutch*, is the dried extract of an East Indian tree, *Acacia catechu*. It contains from 45 to 55 per cent. of a special variety of tannic acid. The extract is evaporated until a thick, dark-brown product is obtained, which solidifies on cooling, and is exported in this form.

Gallnuts, or *nutgalls*, are excrescences on certain plants, caused by gall flies, which puncture the bark in order to deposit their eggs. Oak gall, or Aleppo galls, and Chinese galls are the most important. The oak gall is formed by the insect on *Quercus infectoria*. The eggs hatch and the larva develops

within the gall. The best galls are gathered before the fly becomes fully developed, and contain from 60 to 70 per cent. of gallotannic acid. The Aleppo galls are the most valuable.

Mangrove bark has of late years become popular as a cheap tanning agent. The mangrove tree grows in swamps in tropical and semitropical countries, and the bark contains a quantity of tannic acid, varying with the locality of growth. The African bark is the strongest in tannin, running as high as 45 per cent.; South- and Central-American bark contains as much as 28 per cent., while the Florida bark rarely has more than 22 per cent. of tannin. When used alone, the African bark gives a rather harsh leather of a bright-red color, but it makes an admirable combination with native American barks.

Sumac in all its varieties is a common and valuable tanning agent. It consists of the powdered leaves of the so-called tanners' sumac (*Rhus coriana*, *R. typhina*, etc.). The best sumac comes from Sicily, but Italian, Spanish, French, and American sumac is also found on the market. Sumac contains from 15 to 30 per cent. of a light-colored tannin, which is in great demand in the manufacture of some classes of leather.

Chestnut wood is largely used for extract manufacture in the United States, but, mixed with bark, its use in the tannery leach house is becoming quite common. The wood found in the Northern states contains from 5 to 8 per cent. of tannin, while Southern chestnut wood often contains as high as 11 per cent. of tannin. The chestnut tree, being of quick growth, offers a solution to the problem of offsetting the decrease in vegetable tanning agents. The chestnut blight, however, which has devastated the Atlantic Coast, places this industry in a very serious position, and every effort is being made to check the disease.

Valonia is the commercial name for the acorn cups of several species of oak (*Quercus ægilops* and *Quercus macrolepis*) coming from Asia Minor and Greece. They contain from 25 to 35 per cent. of tannin, somewhat resembling that of oak bark, but giving a browner color and heavier *bloom*. It makes a hard, water-resisting leather and is sometimes mixed with oak bark for use in sole-leather tanning.

Divi divi is the dried seed pods of a South American bush. The pods are about 3 inches long, of a brownish color, and in drying bend in the form of the letter S. These pods contain from 30 to 50 per cent. of a peculiar tannin somewhat similar to that of valonia.

Myrobalans are the dried fruit of several species of *Terminalia* from Hindustan, Ceylon, and other countries. They contain from 28 to 35 per cent. of tannin, and are generally used in combination with other tanning agents. Some varieties cause a bloom similar to that of oak bark, and all varieties are great acid formers in the tan yard.

Mallet bark is an Australian product containing as high as 50 per cent. of tannin similar in color to oak bark.

7. Classification of Tannins.—The tannins in tanning materials are different members of a large group of organic bodies known chemically as *tannic acids*, or *tannins*. They differ widely in chemical constitution and reaction, but all have the common property of precipitating gelatine and forming soluble compounds with animal tissue. They are all compounds of carbon, hydrogen, and oxygen, but their ultimate structure is little understood.

When heated, the natural tannins yield catechol, $C_6H_4(OH)_2$, or pyrogallol, $C_6H_3(OH)_3$, and sometimes both. The classification of tannins on these chemical lines bears out an old classification made on the appearance of the tannage.

8. Tannins were formerly divided into those which yield the whitish deposit on the surface of the leather, called *bloom*, and those which do not. Most tannins that give a bloom to the leather are *pyrogallol tannins;* a solution of their non-tannins when separated has an opalescent appearance. The tannins that give no bloom to leather are classed as *catechol tannins.*

When treated with sulphuric acid, the pyrogallol tannins yield gallic acid or ellagic acid, the latter combining with tannic acid to form the bloom. Under this treatment, the catechol tannins yield the reddish-brown insoluble bodies known to all tanners as *reds*. These reddish-brown insoluble bodies differ from the original tannins in containing fewer molecules of

and the skins become a mass of finer fibers. The lime also saponifies the natural fat, or oil, of the skin.

17. Lime vats are made of timber or of masonry and are sunk into the ground so that the tops of the vats are on a level with the floor. The contents of the vats are made up by slaking the desired amount of quicklime and thoroughly plunging the solution. Generally, two or more lime vats of different ages are used, the hides remaining in one vat for a time and then being moved by means of hand reels between the vats, to the next lime vat.

The time required for liming depends on the kind and condition of skins, conditions of the atmosphere, and the temperature of the limes in use.

The question of when to throw away the limes is also an open one. Some tanners use them until they are almost saturated with decomposing matter extracted from previous hides. A lime in this state becomes a depilator by means of putrefaction and not because of its caustic action, but this should not be considered as good practice.

18. Lime in excess must be present in the vats, so that a saturated solution of the hydrate of calcium is always surrounding the hides. Lime in solution is rapidly consumed in the depilation of the hides and must be constantly renewed. Much of the residue of the lime vats, generally mistaken for unused lime, is in reality a mixture of calcium hydroxide and calcium carbonate formed during the liming process. It is, therefore, found practical to add fresh lime from time to time to the vats and by frequent plungings keep it in suspension.

19. Hydrated Lime.—In place of the older method of using lump lime, many tanners now employ the product known as *hydrated* lime. This form of lime is produced by adding just sufficient water to bring about the union between the calcium oxide and water, according to the following reaction

$$CaO + H_2O = Ca(OH)$$

The advantage of this material, which comes to the tanner in the form of a powder packed in bags, is that it may be kept indefinitely without change, and is always uniform in composition and action.

20. Sodium Sulphide.—Sodium sulphide, when dissolved in water and used as a depilating agent, has the property of quickly destroying hair and epidermis. It has the advantage of rapid action and the production of a tight leather, but has at the same time the disadvantage of a tendency to cause a drawn condition of the grain. For certain classes of leather, its use is desirable, in which case a 20° Bk.* solution is prepared in a paddle at a temperature of 70° F. The stock is entered and the paddle run for about 2 hours, when the wheel is stopped and after that it is run for 5 minutes each hour during the remainder of the day. The stock is kept in the liquor overnight and turned from time to time during the morning. At about noon the plug is drawn and the spent liquor discharged. The paddle is filled with water and run for half an hour. One per cent. of sodium bicarbonate is now added and the wheel turned for the same length of time. Fresh water is then turned on and the stock washed in running water for 3 hours.

Sodium sulphide is sometimes used with lime. It forms caustic soda and calcium sulphide when it comes in contact with the lime. The calcium sulphide acts as a solvent for the hair and renders easier the removal of the very fine hair. The use of sodium sulphide shortens the unhairing process and causes less loss of hide substance as compared with lime, but it has the disadvantage of causing brittle, harsh leather unless it is carefully used in comparatively small amounts. The usual custom is to add the sodium sulphide in the first stages of depilation, the amount employed being about 10 per cent. of the lime taken.

21. Sodium Sulphide and Calcium Chloride.—It has been found that a combination of calcium chloride with

*See *Manufacture of Leather,* Part 2.

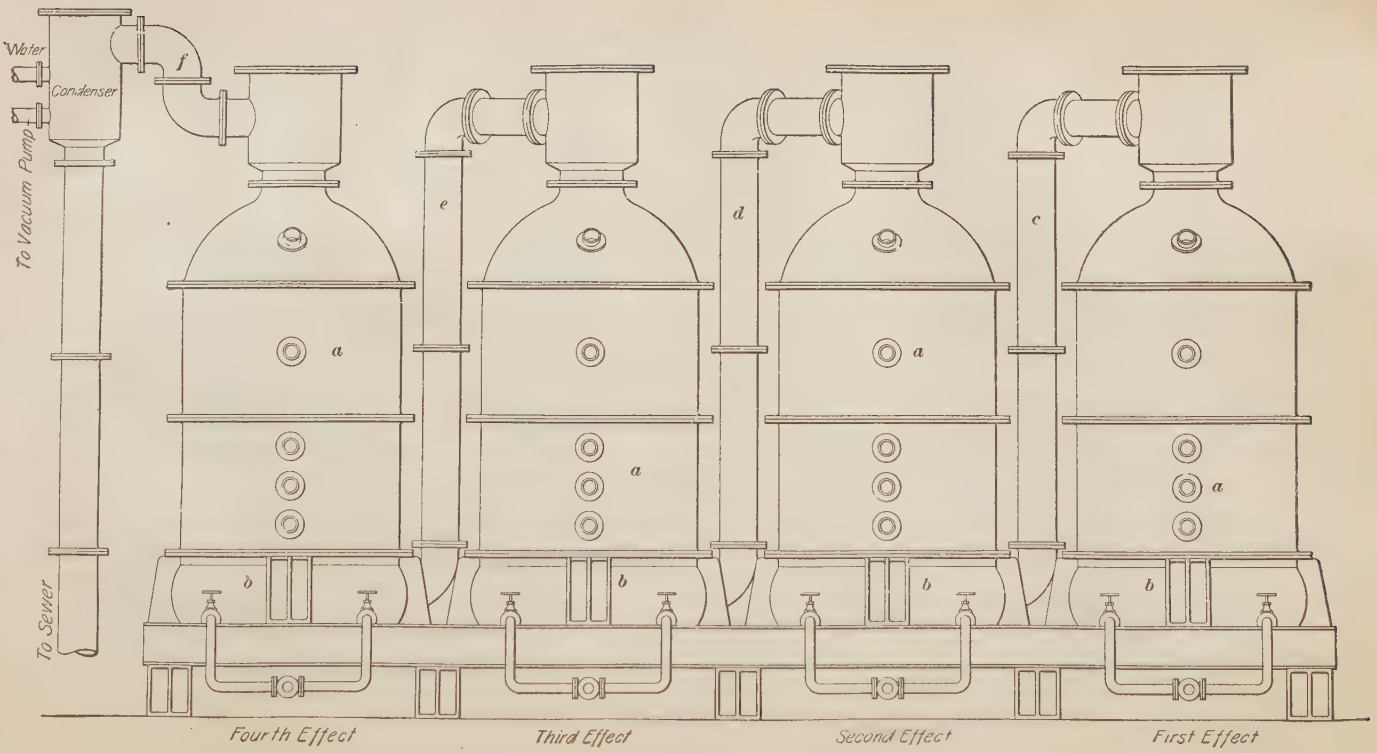

Water
Condenser
To Vacuum Pump
To Sewer
f
e
d
c
a
b
Fourth Effect
Third Effect
Second Effect
First Effect

Fig. 1

lower ends of which are expanded into openings in the upper and lower heads of the drum. The steam drum has a circular well in the center, generally of a diameter equal to one-third the diameter of the drum. The purpose of the well is to help the circulation of the liquors while they are boiling. Vapor pipes lead from the top of the body of one effect to the steam drum of the next, the vapor pipe from the last effect being connected with the condenser. Pipes for conveying the thin liquor to each pan, and for conveying the liquor from one pan to the other, are provided. Pipes for conducting the condensed steam and vapors from the steam drums and for removing the finished extract from the last effect are also provided.

Liquor is put in the pan, condensation water removed from the steam drums, the finished extract removed from the last effect, and the vacuum maintained by different pumps adapted to the work.

12. In operation, the pans are charged with liquor, pumps are started, and steam turned into the steam drum *b* of the first effect; the steam surrounding the multitude of tubes in the steam drum is rapidly condensed, and the liquor in the pan soon begins to boil. The vapor from the boiling liquor passes through the vapor pipe *c* into the steam drum *b* of the second effect, gives up its heat to the liquor in this effect, and is condensed. The vapor from the liquor in the second effect goes through the vapor pipe *d* to the steam drum *b* of the third effect, and the vapor from this effect goes through the vapor pipe *e* to the steam drum *b* of the fourth effect. The vapor from the fourth effect goes through the pipe *f* to the condenser, where it is condensed by a spray of cold water. The condenser is attached to a leg pipe about 35 feet long, having its lower end sealed in a water well overflowing to the sewer; the suction pipe of a vacuum pump is attached to the lower part of the condenser and maintains a vacuum of from 24 to 27 inches of mercury in the condenser and last effect. This lowers the boiling point to such an extent that liquor boils in the last effect at a temperature close to 150° F. Vapor coming from the third effect is quickly condensed in the drum of the fourth effect

and causes a decrease in pressure in the body of the third effect. The boiling point in the third effect is thus lowered, causing a slight vacuum that influences the pressure and boiling point in the second effect, and in turn the condensation of vapors coming into its steam drum is thereby quickened.

The vacuum on the first, second, and third effects is materially increased by the suction of the pump used to remove the condensation from the drums. In practice, it is customary to maintain a steam pressure of 5 pounds on the drum of the first effect, a very slight vacuum in the first effect, and a regular increase in vacuum thereafter, until the maximum is reached in the last effect. The liquor is pumped into the first effect, from which it is sucked to the second, and from the second to the third, and from the third to the fourth, the liquor in all effects being maintained at the desired level by regulating the valves on the pipes connecting the pans, so that enough is admitted to replace the amount evaporated. When the desired concentration is reached, the extract is slowly pumped from the last effect to the clarifying tank, or to the storage tank in case the liquor is not to be clarified.

13. Some extracts are marketed with a specific gravity of 1.22, or 44° Twaddell, others are still further reduced to a specific gravity of 1.26, or 52° Twaddell, while practically all the foreign extracts come to the United States in the solid form, containing from 20 to 25 per cent. water. For evaporating to dryness the strike pan or drum dryer is used.

Hemlock-bark extract has been longest on the market. It is made from the common hemlock bark in localities where hemlock grows plentifully and is shipped to other less-favored points.

Rock-oak bark, *chestnut-oak bark and wood*, *mangrove*, *sumac*, *quercitron*, *mimosa*, *quebracho*, *gambier*, *acacia*, and other woods and barks are extracted, and their extracts form valuable adjuncts to the ordinary tan liquor.

Among American tanners, the standard extracts are quebracho and chestnut wood.

Quebracho extract is made from the wood of the quebracho tree, a close-fibered South American wood. It produces a

fine-colored tannage, but is better adapted to the tanning of upper leather than for sole leather, as its low non-tannin content tends to keep it *sweet;* that is, it does not foster the growth of organic acids necessary to plumping.

Chestnut-wood extract is made from the wood and bark of the chestnut tree, found in nearly all parts of the United States. Used in connection with other tanning materials, it is perhaps the most valuable of extracts. The tree grows quickly, and if the young trees on a stripped tract are forested, the original growth will be duplicated and large enough to cut in 15 or 20 years.

14. Preparation and Leaching of Bark.—The leaching of bark is an operation in tanning which has caused the loss of thousands of dollars through improper manipulation. Even at this late day, tanners are leaving in the cast-off bark as high as 25 per cent. of its original tannin content. When the theory of leaching is thoroughly understood, there will be no such wanton waste.

The principles of saturation and equalization underlie the theory of leaching. A piece of hot iron placed in water loses its heat to the water and becomes colder, while the water is warmed by the iron and finally both iron and water are of the same temperature. The same principle is involved in the process of leaching; both the leach and liquor ultimately become of equal strength. A strong liquor run on a spent leach will come off the leach weaker than when it ran on. In a perfect leaching system, the object is always to run a liquor on a leach that can add tannin to the liquor.

15. Preparation of Bark for Leaching.—Various methods of preparing the bark for leaching are in use. They all consist of some kind of grinding and shredding. Proper preparation of the bark is important and quite essential to close leaching; the best leaching system will not produce good results unless the bark is reduced to such a state that the water or liquor can readily penetrate to every fiber.

Mills for grinding bark have the common feature of a revolving disk into which cutting knives are set radially. Most of

them have a secondary disk that completes the work which the first disk started; the bark then passes through small apertures to a conveyer.

16. Ott Bark Mill.—The Ott mill, shown in Fig. 2, is the most popular of the grinders. It consists of a hopper *a*,

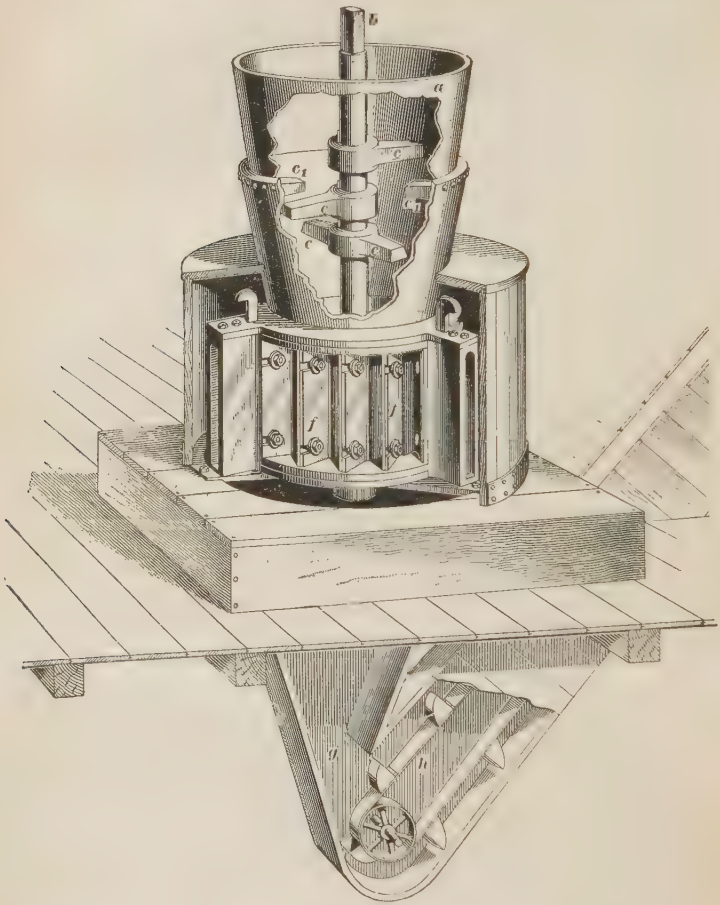


Fig. 2

leading to the lower part of the mill, where the grinding is done. A shaft *b*, by means of which the mill is driven, runs

through the center of the entire mill, which may be driven by it from either the top or the bottom. The portion of the shaft running through the hopper has keyed to it four projecting iron arms c, which, with the aid of similar projections c_1 from the inner sides of the hopper, break the bark into small pieces that fall into the runner, or carrier, shown in Fig. 3 (a). The runner, or carrier, consists of a circular piece of steel d fitting the lower part of the mill; it is attached to and revolves with the shaft that passes through its center. Attached to the shaft above this disk are four angular iron wings e that

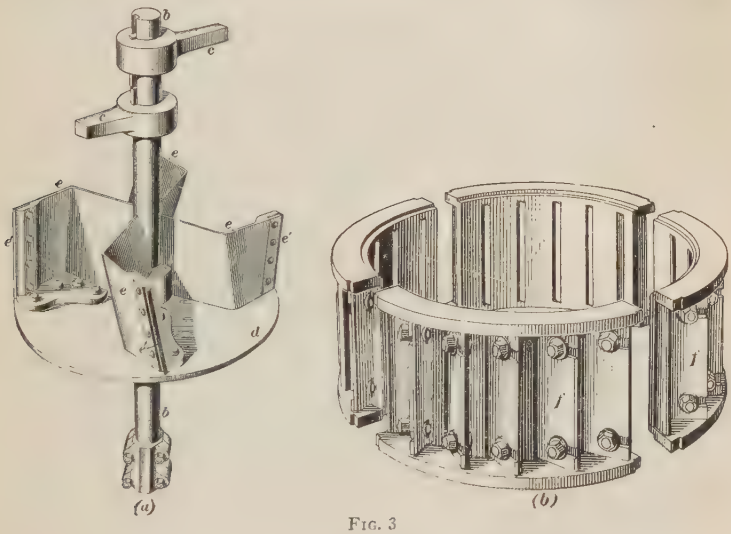


Fig. 3

extend to the edges of the disk and are attached to it by bolts engaging the flanges of the wings. The ends of the wings are supplied with steel tips e' that form a cutting surface. The knives f, Fig. 2, are set vertically and bolted to a slotted cylinder of the same height as the runner, and surrounding it. The bark, having been broken by the upper arms, falls into the runner and is ground by being carried against the knives by the steel-tipped wings. Passing through the knife slots, the bark falls into the bottom of the grinder and is delivered by means of a spout g to the carrier h, which takes it to the leach house.

The cylinder, shown in Fig. 3 (*b*), containing the knives *f*, is made in segments that can be removed for the grinding and setting of the knives, five of which are held in each segment. The mill is run at a speed of 100 to 150 revolutions per minute; the knives require grinding and setting at intervals which depend on the character of the material that is ground.

Many tanners prefer a shaving machine that reduces the bark to shreds instead of grinding it. With oak bark it gives better results than the ordinary grinder.

17. Williams Patent Bark Shredder.—The machine shown in Fig. 4 is the best known form of the shaving, or

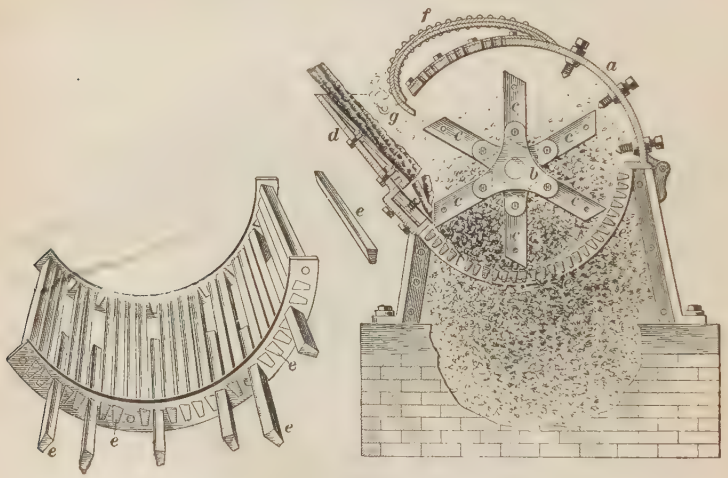


Fig. 4

shredding, type of machine. It is cylindrical in shape, the casing *a* surrounding a horizontal shaft to which a hub *b* is keyed. Heavy, sharp-pointed arms, or hammers, *c* that present a cutting edge, are hinged to the hub by pinions, and when the shaft is in motion the centrifugal force causes them to radiate from the hub. The hopper *d* is at the side, the floor of the hopper being inclined by a raised plate, the end of which forms a sharp breaking corner so that the bark is cut in small pieces before the final shredding takes place. A segment of a cylinder, shown at the left in Fig. 4, contains the knives *e*

and is so placed beneath the revolving arms that the edges of the knives and the sharp ends of the revolving arms form shears and cut or shred the bark forced between them. The shredded bark then falls between the knives into the conveyers. The segment, or *cage*, containing the knives is in the form of a semicircle, and the knives are so arranged that the lip, or projecting edge, presents a shaving, or shredding, surface rather than a pulverizing surface. The knives can be taken from the cage, resharpened, and replaced. A bowed steel shell *f*, with one edge riveted to the top of the casing and the other edge projecting through the hopper opening into the cylinder, forms a chamber for the settling of the dust after it has been moistened by a spray of steam introduced at the side of the hopper at *g*. Economy of power with greater grinding capacity is claimed for this type of machine; it is especially valuable for wood and barks of a fibrous nature.

When ground, the bark is conveyed to the leach house by a mechanical conveyer or blower, the former being the cheaper method of conveyance.

18. Vat Leaching.—Most of the older leach houses were constructed by sinking the vats in the ground. While this method seems to economize the heat used in latter-day leaching, inability to repair leaks is a serious objection to this form of construction, and all the newer types of leach houses are constructed with the bottoms of the vats above ground. In this way, leakage is detected and stopped, and the spent, or exhausted, tan is much more easily removed from the leaching vats. Mechanical contrivances for handling the bark before and after leaching are in general use. The vats, or *leaches*, are filled from an overhead conveyer leading from the bark storehouse; and when the bark has been leached, the spent tan falls through an opening in the bottom of the vat into a conveyer that takes it to the furnace, where it is used as fuel.

The vats used for leaching are usually arranged and worked in sets; the vat containing the freshest bark is known as the head-leach and that containing the nearly spent bark is called the tail-leach.

The vats, or leaches, arranged in sets or sections are provided with perforated false bottoms, and they are so piped that the liquor from the bottom of one leach is delivered to a box on the top of the next leach in the section and falls either directly on the bark or is distributed over its surface by means of an arrangement known as the *sprinkler*. The sprinkler is made of two pieces of brass pipe screwed into a tee, which, by means of a swivel joint, is connected with the pipe leading down from the box on top of the leach. Each arm of the sprinkler has a row of perforations, and the ends of the arms are closed by removable caps to allow cleaning. The perforations on one arm are opposite those on the other, so that when liquor flows through the box into the sprinkler one arm delivers liquor in one direction, and the other arm delivers it in the opposite direction. This causes the sprinkler to revolve and spread the liquor over all parts of the bark.

19. The general scheme for leaching with vats is to run water on the tail-leach, and after the liquor comes off it is put on the next, and so on throughout the set until the liquor comes off the head-leach, when it is sent to the settling tanks or storehouse. The tail-leach, after receiving all the water intended for it, is emptied or *pitched*, filled with fresh bark, and becomes the head-leach, the leach next above it becoming in turn the tail-leach.

This method of handling the liquors is common to all systems of vat leaching. It is in the method of applying the water, of removing the liquor from leach to leach, the temperature of the liquors, the depth of the vats, and in many other minor details that the various systems differ.

With some systems, the use of warm liquors on every leach is advocated, the water going on the tail-leach being as near the boiling point as possible; the water becomes cooler as it goes to the next leach and finally becomes too cool, in the judgment of the advocates of this system, and is reheated.

Some leaches have steam coils, protected from the bark by a false bottom, in order to maintain the temperature deemed necessary for proper leaching. Other leaches have in the box

on the top of the leach a coil of steam pipe for heating the liquor from the preceding leach. Hot leaching, if not carried to extremes, is the most economical method. When the continued use of very hot waters is resorted to, the reds and the resinous matters of the bark are dissolved in the liquor. These reds are of no use in tanning operations, and serve to make an impure liquor, because their proportion to the amount of tannin that is removed by the extra heat is altogether too large to be economical.

Within certain limits, the higher a column of bark through which a liquor passes, the stronger is the liquor and the more perfect the leaching; the weight of the column is limited by its interference with the circulation of the liquor. When the leach is too deep, the bark packs down tightly and stops the even percolation of the liquor.

20. In some systems of leaching, the liquors are moved from leach to leach by pumps worked by a common rod. The conditions, however, are not the same in each leach, and hence pumping devices should be fitted to each leach separately, so that the regulation of their speed may be under control.

The *air* system of handling leach-house liquors is now quite common, and it is probably the best method of moving these liquors. Compressed air is admitted to the bottom of the upright pipe that conveys the liquor from the bottom of one leach to the top of the next, and raises the column of liquor in the pipe until it flows into the liquor box on the top of the next leach.

The practice in some tanneries is to empty a leach of liquor entirely and then run on more liquor. The leaches should be kept covered with liquor at all times. If one is drained free from liquor, the bark settles down and packs tightly; the liquor running on the bark in this state channels its way to the bottom and uniform percolation is not secured.

A constant and slow influx of liquor on the leach is preferable to a large stream. The liquor should be given a long contact with the bark. It should be delivered on the top of the leach in a divided stream and not in a single strong jet. Liquors that are partly spent are frequently returned to the leach

house in order to be strengthened and to keep up the general strength of the leach-house liquors. The returned liquors are generally run on the upper leaches of the section, as the lower leaches, being nearly spent, would take strength from, instead of adding strength to, the liquor. While the partly spent liquors have lost a considerable share of their tannin during the tanning operations, they still retain a large proportion of their original non-tannin content; when strengthened, therefore, they do not represent the tannin strength that is possessed by a new liquor of the same specific gravity.

21. A complete description of a leaching system will give a general idea of the mode of operating. The leaches are circular in form, 12 feet in diameter, and 15 feet deep, with plank covers, and with heater boxes on top of them. The liquors are moved by means of the air system. Water as near a temperature of 212° F. as possible is run on the tail-leach, from the bottom of which it is pumped to the heater box of the next leach. Here it is reheated while passing over the steam coils and falls through a pipe into the leach. The liquor passes through each leach successively and is reheated until it reaches the leach next to the head-leach. Here, it is not reheated, but passes through the bark and comes into the box on the head-leach at about 150° F. The sprinkler used on the head-leach distributes the liquor over the surface of the bark. When the head-leach is *wet down* or filled with liquor, the liquor is run off to the *cooler* or storage vats. The pumping from this head-leach is continued until the liquor becomes too weak for use in the tannery. When used yard liquors are returned to the leach house, they are pumped into the heater box on the top of the head-leach, heated, and distributed over the bark by the sprinkler. After all the returned liquor has gone into the heater box, the liquor from the leach next to the head is pumped into the head-leach and the regular leach-house process continues.

The bark in the leaches is kept covered with water or liquor at all times, and the pumping from one leach to the next is regulated with this end in view.

The preceding remarks on leaching apply particularly to the leaching of such common barks as hemlock and oak, but with other materials the general principles are the same, and, except for variations in the size of leaches and in the temperature of operation, the method of procedure is similar.

22. For some materials rich in tannin, *autoclaves*, or metallic cylinders, in which the leaching is carried on at different pressures, are used. Drum-leaching systems have been used on oak and hemlock barks, but for these materials they are not necessary; drum systems have been very successfuly used in the leaching of some high-priced imported barks and woods containing high percentages of tannin.

23. Density, or Specific Gravity, of Tan Liquors. The density of tan liquors is determined by means of a form of hydrometer called a *barkometer* and having a graduated scale showing *degrees barkometer*, or, as it is generally written, degrees "Bk." One degree Bk. represents the density of a liquor having a specific gravity of 1.001, barkometer degrees being the decimal portion of the specific gravity figure read in thousandths; thus, 10° Bk. is specific gravity 1.010, 45° Bk. is specific gravity 1.045, etc.

A barkometer merely shows the density of a liquor, or its weight compared to that of water; it cannot determine the tannin strength of a liquor, as one 20° Bk. tan liquor might contain 3 per cent. of tannin and another liquor of the same density might contain only 1.5 per cent. of tannin. Non-tannins and other soluble constituents of tan liquors influence the density, and hence the mistake should not be made of considering a 25° Bk. liquor necessarily stronger in tannin than a 20° Bk. liquor. The barkometer readings should be made with the liquor at a temperature of 60° F., or else a correction should be made to compensate for the expansion or contraction of the liquor. If warmer than 60°, the liquor will show less barkometer strength; if colder, it will show more, so that all readings should be made at, or corrected to, 60° F.

The specific gravity of an extract is generally denoted in degrees Twaddell. One degree Twaddell is equivalent to a

specific gravity of 1.005, being one-fifth of the decimal portion of the specific-gravity figure when the latter is represented in thousandths. Thus, specific gravity 1.225 is 45° Twaddell, specific gravity 1.400 is 80° Twaddell, etc. From this relation, it is evident that 5° Bk. is equal to 1° Twaddell, or 45° Twaddell is 225° Bk.

ANALYSIS OF TANNING MATERIALS

24. The methods of analysis for tanning materials have been gradually developed and are peculiar to this class of work. In addition to the general laboratory equipment of apparatus and chemicals, there are needed special contrivances and preparations, such as extraction apparatus, devices for shaking, animal charcoal, and a supply of hide powder.

ANALYSIS OF BARK, WOOD, ETC.

25. Preparation and Extraction of Sample.—The sample is ground so that it will pass through a sieve having 20 meshes to the linear inch. It is well mixed, and a 10-gram sample is dried overnight in a steam oven for moisture determination. A weighed portion of the bark is then extracted in some form of extractor suited to the nature of the material under examination. In all cases, the extractor should be of such form as to permit the removal of the first, or strong, portions of the extractives, so that these will not be subjected to the influence of sustained high temperatures. For materials like oak and hemlock bark or chestnut wood, a different method of extraction from that required for sumac, algorahilla, etc., may be used.

26. The Reed Extractor.—An extracting apparatus suited for use on all materials is that known as the *Reed extractor*, which is shown in Fig. 5. By varying the method of operation, practically all tanning materials may be extracted by it. For use on sumac or like materials, which do not allow of an initial extracting temperature of boiling water, the material is weighed into a cup *b* that has a perforated brass

bottom and rests on a perforated plate *d* of the outer vessel *a*. Water is placed in the vessel *a* surrounding the cup *b* and is kept at the desired temperature by heat applied to the bottom of *a*. Suspended over cup *b* is an inverted vessel *c* filled with water and having an outlet *e* at a higher level than that of tube *f*.

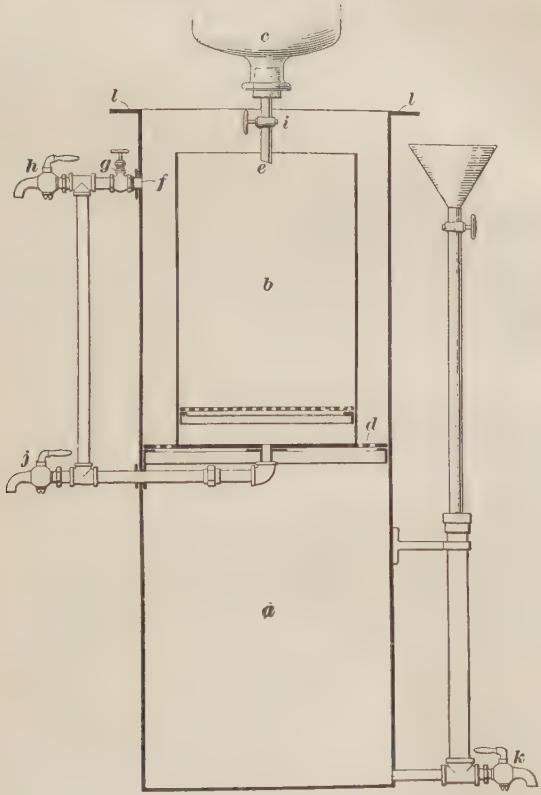


FIG. 5

Cocks *g* and *h* are closed and cock *i* is opened, and water is allowed to flow into the cup. When the desired temperature is attained, cock *j* is partly opened and percolation begins, the extractives being delivered through cock *j* at any desired speed, additional water flowing from *c* as the level falls below the opening *e*. When the strong extractives have been removed,

cock *j* is closed and some of the water surrounding *b* is drawn off through cock *k* until about 600 cubic centimeters of water remains in the bottom of *a*. The inverted vessel *c* is removed and to the flanges at *l* is attached a conical cap to the apex of which a condenser tube is brazed. An annular ring fitted to the interior surface of the cap serves to guide the water of condensation, so that it falls into the cup *b*.

The water in *a* is then boiled and the condensed steam falling into the cup *b* completes the extraction. The extractives may be delivered directly by closing cock *g* and opening either *h* or *j*. If continuous operation is desired, cocks *h* and *j* are closed and cock *g* is opened, and the extractive is returned to the lower part of *a*.

27. The Teas Percolator Extractor.—The Teas percolator extractor, shown in Fig. 6, may be used on all new materials, but a large volume of weak extractive solution results if used on spent or leached materials. It consists of small cylinders surrounded by a heating jacket *a*, the latter being supplied with water from a reservoir through *b*. The reservoir is located above the apparatus so that, when desired, the boiling point of the water may be raised above the normal boiling point. In operation, the perforated disks on the ends of brass rods *e* are covered with a thin layer of cotton or filter paper and the weighed material is brushed or washed into the cylinder and covered with water. Heat is applied to the bottom of the jacket, and when the desired temperature is attained, the cocks *c* are opened and hot water allowed to drip on the material. The extracted material is delivered through any of the cocks *d*, depending on whether a flooding or a time percolation is desired. After the first portions of the extractives are removed, the heat is raised to the boiling point and the extraction completed.

28. The Teas Cumulative Extractor.—For all spent materials, as well as new materials, like oak and hemlock bark, etc., the Teas cumulative extractor, shown in Fig. 7, is more convenient than the percolative extractor described in the preceding article. The cumulative extractor may also be used on

sumac and similar materials by varying the method of operation. In using this extractor, the stem *e* is connected to a copper or glass flask and the cap *d* to a condenser. The cock *f* and side openings *h* and *j* are closed. The material is weighed or washed in after covering the perforated plate at the bottom with a thin layer of cotton or filter paper, and then thoroughly moistened. A liter of water is placed in the flask, the apparatus connected up with the flask and the condenser, and heat applied to the bottom of the reservoir. The lower side opening *h* is opened, and the first portions of the extractives are collected there. After the strong extractives have been removed, the side opening is closed and the cock *f* opened, and a cumulative extraction continued until extraction is complete.

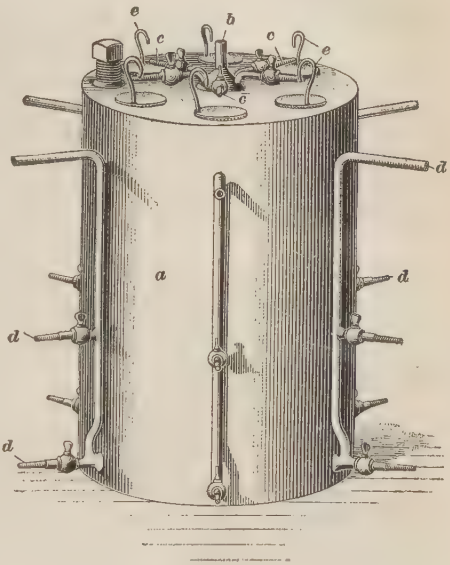


Fig. 6

29. In extracting sumac and similar materials, which must have cooler initial extraction temperatures, the cap can be left off and water at the desired temperature allowed to drip on the material, collecting extractives at either side opening. When the strong portions have been removed, the cap is replaced, connected with the condenser, the side openings closed, the cock *f* opened, and the extraction completed with steam from the flask connected to the stem *e*. The materials mentioned may also be extracted by covering them with cold water almost to the level of the upper side opening, connecting with condenser and reservoir, boiling the water in the reservoir slowly, and collecting the first portions at the *upper* side opening *j*.

When the desired amount of extractives is thus removed, the side opening is closed, the cock *f* opened, full heat applied to the reservoir, and extraction completed.

In all cases where strong extractives are removed from the apparatus, they should be mixed while hot with the weaker extractives that have accumulated in the reservoir, the entire extraction allowed to cool, made up to 1,000 cubic centimeters, and the analysis proceeded with.

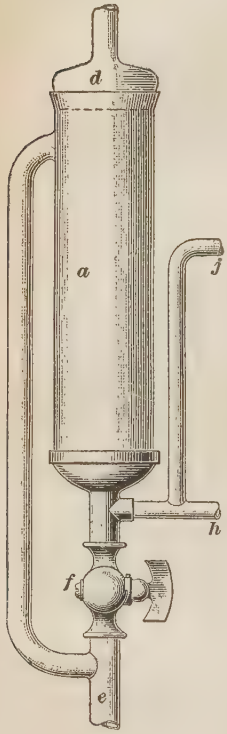


Fig. 7

30. Remarks Regarding Determinations to Be Made.—Three determinations, the *total solids*, *soluble solids*, and *non-tannins*, are made in a tannin analysis, and from the results the *insolubles*, or *reds*, and the *tannins* are obtained. The difference between the total-solids figure and the soluble-solids figure gives the amount of insolubles, or reds. By subtracting the non-tannin results from the soluble-solids results, the amount of tannins in the liquor is obtained. It is not necessary to dwell on the definition of these terms, but a few words on some of their constituents will not be amiss.

31. The reds, or insolubles, have been defined under tanning materials. Because of their greater or less solubility in warm liquor, it is necessary that the analysis should always be made when the liquor has a temperature of from 60° to 70° F. If colder, the reds figure will be higher and the subsequent tannin result lowered; if warmer, the reds will decrease and the tannin content increase.

Under non-tannins are classed all soluble substances in the liquor not absorbed by hide. For the most part, the non-tannins consist of sugary substances derived from the sap of the tree. In the same manner, under tannins are included

all soluble substances that will combine with hide, thus embracing all the forms of tannic acid.

32. Determination of Total Solids.—When the liquor, extracted and prepared as has been described, has cooled to 20° C., the cylinder *a*, Fig. 7, is shaken and allowed to stand for $\frac{1}{2}$ hour; this is to allow small particles of bark to settle, so they will not be counted as reds, or insolubles proper. At the expiration of $\frac{1}{2}$ hour, remove with a pipette 100 cubic centimeters of the liquor, place in a weighed glass crystallizing dish, and evaporate to dryness in a combined evaporator and dryer. Cool in a desiccator and weigh. From this weight the percentage of total solids is determined.

33. Determination of Soluble Solids.—To determine the soluble solids, place 1 gram of kaolin in a beaker and add 75 cubic centimeters of the tannin solution. Stir and pour on a pleated filter paper, collecting the filtrate in a clean beaker. Then return the filtrate to the paper for 1 hour, keeping the filter full. At the expiration of 1 hour, remove any of the solution remaining in the funnel and throw away both the solution and the filtrate. Refill the filter with the tannin solution, and as soon as the filtrate runs clear, collect it in a clean, dry beaker and remove 100 cubic centimeters for evaporation and drying. The kaolin should be previously washed with hydrochloric acid, then with distilled water, and finally dried and pulverized. It is used as an aid in filtering, forming a thin film over the paper, thus insuring a clear filtrate. The paper and kaolin absorb tannin from the solution, so that the affinity of these for tannin must be satisfied by allowing them to be in contact with the tannin solution for 1 hour before filtering the solution to be collected for drying and weighing.

34. Preparation of Hide Powder for Determining Non-Tannins.—To determine the non-tannins, hide powder is used. Hide powder is made by liming and depilating selected steer hides, neutralizing the lime remaining in the hide, and washing out the excess of acid with water. The

hide is then slowly and carefully dried without heat, and, when dry, it is ground about as fine as sawdust.

To prepare hide powder for use, the almost universal practice is to chrome it slightly. The chroming treatment increases the rapidity of absorption of the tannins, and by combining with the chrome-tanning materials the soluble portions of the hide substance are rendered insoluble. The American method of chroming is first to soak the dry hide powder overnight in water and then squeeze out the soak water through a linen cloth. Fresh water approximating twenty-five times the weight of the dry hide powder is added, and chrome alum (in solution) to the amount of 3 per cent. of the weight of the dry hide powder is added and thoroughly mixed. The mixture is frequently stirred during the day, allowed to stand overnight, and washed the next morning by alternately squeezing through a cloth and adding fresh water until the wash water is free from sulphates. When thoroughly washed, the mass is placed in a press and squeezed until the wet hide contains between 70 and 75 per cent. of water. It is then ready to be used for detannizing the tannin solutions.

35. Determination of Non-Tannins.—For the non-tannin determination, measure 200 cubic centimeters of the bark liquor into a strong glass tumbler, such as is used with a milk-shake machine, and after weighing 20 grams of the wet hide, place the liquor in the steam oven and dry it for moisture determination. Weigh out from the press the amount of wet hide necessary for the determination of non-tannins. Place this in the liquor, breaking up the lumps with a glass rod, and then shake the solution thoroughly. The shaking may be done by hand, using a tin cap such as is used for mixing drinks, or by a hand- or power-driven milk-shake machine. Shaking for 5 minutes on a milk shaker is sufficient for the hide powder to absorb every trace of tannin from the liquor. After shaking, add about 2 grams of kaolin and filter the solution through double filter paper. When the filtrate is running clear, collect, and with a pipette remove 100 cubic centimeters to a crystallizing dish; evaporate, dry, and weigh

in the same manner as when the percentage of solids was determined.

The amount of hide powder to be used depends on the strength of the bark liquor. In the case of unleached materials, the amount of sample extracted and the proportion of extraction water should be such as to give between .35 and .45 gram of tannin per 100 cubic centimeters of extractive solution. If these specifications have been carried out, an amount of wet hide powder representing from 12 to 15 grams of the dry powder should be used for 200 cubic centimeters of solution. In extracting spent materials, it is seldom found possible to procure an extractive solution that will contain .35 to .45 gram of tannin per 100 cubic centimeters, but the proportion should be approximated as closely as possible, and the quantity of hide powder used should be decreased accordingly.

Whether or not enough hide powder has been used, can generally be judged by the appearance of the non-tannin filtrate; if clear and white or pale yellow, the tannin has probably been removed. If the filtrate has a red or brown tinge, it is generally safe to assume the presence of some tannin. Doubtful filtrates should be tested with a 1-per-cent. gelatine to 10-per-cent. salt solution, cloudiness indicating the presence of tannin.

36. Calculation of Results of Bark Analysis.—Divide the weight of the total-solids residue by the number of grams of bark taken, and divide this result by the percentage of actual bark in the sample, found by subtracting from 100 the percentage of moisture, as determined in a 10-gram moisture sample. This result, when pointed off to correspond to the decimal part of the original liter, is the percentage of total solids. The percentage of total soluble solids is found in the same manner.

Because of the water added by the wet hide used in the non-tannin determination, a correction must be made. If the 20-gram sample of wet hide powder when dry weighs only 6 grams, there are 14 grams of water added to the liquor for every 20 grams of wet hide used. If 40 grams of wet hide is

used, there are 28 grams of water added, and the volume then becomes 228 cubic centimeters instead of the 200 cubic centimeters originally taken; 100 cubic centimeters of the diluted filtrate has been dried, and it accordingly represents only $\frac{100}{114}$ of the actual amount of non-tannins, so the weight must be multiplied in this case by 1.14. Therefore, to calculate the percentage of non-tannins, divide the non-tannin weight successively by the number of grams of bark taken and the percentage of dry bark, as under the solids calculations, and multiply this result by the hide-moisture correction.

ILLUSTRATION.—For the analysis, 25 grams of bark were taken and 40 grams of wet hide powder were used. The bark contained 12 per cent. of moisture and 88 per cent. of dry bark. A 20-gram sample of wet hide when dried weighed 7 grams. The 40 grams of hide used, therefore, contained 14 grams of dry hide and 26 grams, or cubic centimeters, of water, which latter was added to the original 200 cubic centimeters.

$$\frac{200+26}{200}=1.13, \text{ or the hide-powder correction for moisture}$$

	GRAM
Total-solids residue weighed	.4983
Total soluble-solids residue weighed	.4012
Non-tannin residue weighed	.1441

For the total-solids determination, 100 cubic centimeters of liquor was taken, or .1 of the liter. The calculation would be as follows:

$$\frac{.4983\times100\times10}{25\times.88}=22.65 \text{ per cent. of total solids}$$

The total soluble solids are calculated in the same manner.

$$\frac{.4012\times100\times10}{25\times.88}=18.24 \text{ per cent. of total soluble solids}$$

The total solids less the total soluble solids give the amount of insolubles.

$$22.65-18.24=4.41 \text{ per cent. of insolubles}$$

For the determination of non-tannins, 100 cubic centimeters, or $\frac{1}{10}$ liter, of liquor was dried. The hide-powder correction was found to be 1.13. The calculation would be as follows:

$$\frac{.1441\times100\times10\times1.13}{25\times.88}=7.40 \text{ per cent. of non-tannins}$$

The total soluble solids less the non-tannins give the amount of available tannin.

$$18.24-7.40=10.84 \text{ per cent. of available tannin}$$

The complete analysis is as follows:

					Per Cent.
Total solids	Total soluble solids	Non-tannins	7.40	18.24	22.65
		Tannins	10.84		
	Reds, or insolubles			4.41	
Insoluble parts of bark (not removed by leaching)					77.35
Total					100.00

This would be reported as follows:

	Per Cent.
Moisture	12.00
Total solids	22.65
Soluble solids	18.24
Non-tannins	7.40
Tannins	10.84
Reds (or insolubles)	4.41

37. The figures in the preceding illustration are, of course, on an absolutely dry basis. If it were desired to report the results on the commercially dry basis, simply multiplying the absolutely dry figures by .88 would give the commercially dry figures. The sample having contained 12 per cent. of moisture, there would, of course, be 88 pounds of absolutely dry bark in every 100 pounds of the commercial article.

It is customary to report fresh-bark results on the absolutely dry basis, and then give the tannin figure also on the commercially dry basis. Spent-material results should be reported on the dry basis and cannot really be reported on the commercial basis unless the analysis of the original new material is known. This is because a considerable portion of a new bark is removed by the leaching process, and the analysis of the spent bark is not on the same basis as to bark weight as was the analysis of the original new bark. Taking this into account and figuring back the results to the same basis, the commercially dry tannin figure of a spent tan analysis is found to be about 77 per cent. of the absolutely dry tannin figure.

ANALYSIS OF TANNING EXTRACTS

38. The exact conditions to which an extract analysis must conform, in order that it may be said to have been made by the Official Method, are set forth annually in the report of the American Leather Chemists' Association, which comprises practically all the leather chemists of the United States. As now carried out, the method is to dissolve a quantity of the extract as will give from .35 to .45 gram of tannin per 100 cubic centimeters of solution in 900 cubic centimeters of water at 80° C., making up to the liter mark after standing not more than 20 hours and not less than 12 hours. The temperature of the solution must not go below 20° C.

39. Total Solids.—Mix the solution thoroughly, and pipette 100 cubic centimeters into a tared glass dish. Evaporate, dry, and weigh.

40. Soluble Solids.—Place 1 gram of acid-washed kaolin in a beaker and add 75 cubic centimeters of the solution. Stir and pour on a No. 590 S. & S., 15 centimeters, pleated filter paper. Return the filtrate to the paper for 1 hour, keeping the filter full. At the expiration of 1 hour, pour the remaining solution from the filter or remove with a pipette. Then refill the filter with another portion of the solution brought to a temperature of 20° C., and begin to collect the filtrate as soon as it runs clear. Pipette 100 cubic centimeters of the clear filtrate into a tared glass dish, and evaporate, dry, and weigh. The funnels and receiving vessels should be covered to guard against evaporation.

41. Non-Tannins.—Add to 200 cubic centimeters of the solution a quantity of wet hide powder representing from 12 to 15 grams of dry hide. Shake for 10 minutes and squeeze immediately through a linen cloth. Add 2 grams of kaolin to the filtrate, stir, and filter through a folded filter of size sufficient to hold entire filtrate, returning the filtrate until it is running clear. Evaporate and dry 100 cubic centimeters of this filtrate. The hide powder is to be prepared as previously

described, and the non-tannin filtrate should be tested for tannin if its presence is suspected.

42. Calculation of Results of Tanning-Extract Analysis.—The results are calculated by dividing the different weights by the amount of extract taken and pointing off for the percentage basis, not forgetting the hide-moisture correction on the non-tannin weight.

ANALYSIS OF TAN LIQUOR

43. Determination of Specific Gravity and Total Solids.—Shake the sample well and with a barkometer determine its specific gravity in degrees barkometer. As a general rule, 1° barkometer represents .25 per cent. of total solids, and by applying this rule, the amount of liquor to be taken to make the proper dilution for analysis may readily be computed. The liquors should be diluted so that 100 cubic

TABLE II

AMOUNT OF HIDE POWDER REQUIRED FOR DIFFERENT TANNIN STRENGTHS

Tannin Range per 100 Cubic Centimeters	Dry Hide Powder per 200 Cubic Centimeters
.35 to .45 gram	8 to 10 grams
.25 to .35 gram	5 to 8 grams
.15 to .25 gram	2 to 5 grams
.00 to .15 gram	0 to 2 grams

centimeters of the diluted liquor will give a residue approximating .7 gram in weight. The water used for dilution should have a temperature of 70° F. After thoroughly mixing the diluted liquor, the total solids, soluble solids, and non-tannins are determined as under Analysis of Tanning Extracts. Since the dilution varies with the gravity of the liquor, the tannin strength of the different diluted liquors is not the same, and different amounts of hide powder are used, depending on the tannin content of the liquor.

Table II shows what is believed to be the proper amounts of hide powder to be used for different tannin strengths.

For convenience in calculating results, it is best to dilute the liquors to the volume of 1 liter. When thus diluted, the weights of the different residues divided by the number of cubic centimeters of liquor diluted to 1 liter will give a result that only needs proper decimal pointing to indicate the percentage of each item. The moisture correction for the hide powder must be applied to the non-tannin weight.

44. Determination of Total Free Acids.—There are several methods in use for the determination of the total free acids, but none is above criticism and results are comparative rather than absolute.

Charcoal Method.—To 100 cubic centimeters of the diluted liquor used for the determination of the tannin, add 2 grams of chemically pure animal charcoal. Stir frequently during a period of 2 hours, strain on a dry filter, and titrate an aliquot portion with decinormal alkali, using phenol-phthalein indicator.

Or, to 100 cubic centimeters of the diluted liquor in a flask with a tube condenser add 2 grams of the charcoal. Heat to boiling with frequent shaking; then cool, filter, and titrate an aliquot portion.

Quinine Method.—Dilute 50 cubic centimeters of original liquor to 500 cubic centimeters. To 200 cubic centimeters of the diluted liquor, add 20 cubic centimeters of quinine solution. Mix thoroughly and filter. Take 100 cubic centimeters of the filtrate and titrate with decinormal alkali and phenol-phthalein indicator. Multiply the number of cubic centimeters used by .066 to obtain direct the percentage of acid, as acetic acid, in the original liquor.

The quinine solution is made by dissolving 15 grams of quinine (pure alkaloid) in 110 cubic centimeters of 95-per-cent. alcohol that has previously been neutralized. To this, add slowly while stirring 90 cubic centimeters of distilled water, so as to bring the volume up to 200 cubic centimeters.

Lime-Water Method.—Titrate 20 cubic centimeters of the original liquor, filtered, with twentieth normal lime water.

The end point is indicated by the beginning of turbidity, when sufficient lime water has been added. Some chemists put the filtered liquor in a flat 2-ounce panel bottle, in which the panels are very close, and then titrate, holding the bottle against a strong light.

45. Determination of Combined Sulphuric Acid. In acid tanneries, a determination of the free and combined sulphuric acid present in the liquors is frequently required. To determine the combined sulphuric acid, evaporate 100 cubic centimeters of the original liquor in a platinum dish and char the residue at a very low red heat. Cool, add hydrochloric acid and hot water, filter, and determine the sulphates in the filtrate with barium chloride, as explained in Quantitative Analysis.

To determine the total sulphuric acid, take 50 cubic centimeters of the original liquor, add distilled water and a little hydrochloric acid, bring to a boil, and precipitate the sulphuric acid with barium chloride. The difference between the percentages of total acid and combined acid will be the approximate free sulphuric acid in the liquor.

When the amount of free sulphuric acid only is required, a more accurate method is to evaporate 100 cubic centimeters of the liquor on a steam bath and digest the residue with absolute alcohol, determining sulphuric acid in the alcohol after digestion.

46. Bleach Liquors.—It is frequently desirable to know the amount of material removed from leather by the *bleach* baths. The following method gives fairly accurate figures:

Take samples of all baths before starting the day's work and at the close of the day. Evaporate and dry 50 cubic centimeters of each sample, weigh, and subtract the combined *morning* percentages from the combined *evening* percentages. Multiply the difference in percentages by the weight of water in a single vat, and from the result subtract the weights of soda and acid added during the day (acid weights should be taken at 100 per cent. and sal soda weights at 40 per cent. actual solids). The remainder will be the approximate amount of

organic material removed in all the vats. When this figure is divided by the number of sides bleached, the amount of solids removed from each side of leather will be obtained.

A method of determining the amount of tanning material removed by the soda vat is to evaporate and dry 50 cubic centimeters of the liquor in a platinum dish, weigh, and then char the contents, break up the charred mass, add hot water and titrate. The difference between the weight of the dried residue and the weight of the alkali (figured in its form at the drying temperature), will give the organic matter in 50 cubic centimeters, and knowing the size of the vat and the number of sides bleached, the amount removed per side may be readily calculated.

ANALYSIS OF LEATHER

47. For many reasons, it is frequently desired to determine quantitatively the constituents of different leathers, and while the analysis of leather is not difficult, yet, in order that different analysts may secure concordant results, it is necessary for them to follow identical methods in determining the composition of leather.

The samples should be taken from different parts of the side of leather, since different portions of the leather will show a difference in composition, because of the difference in the thickness and texture of the hide. The belly and flank, being softer than the back, will make leather of an entirely different composition from that of samples taken from the back of the same side of leather.

The samples are prepared by grinding, or by shaving with a carpenter's plane, or by the use of a coarse wood rasp. The finely divided leather should be well mixed and stored in a stoppered glass jar.

48. Determination of Moisture.—In determining the amount of moisture present, 10 grams of the ground leather should be dried for 1 hour in an oven at a temperature of 105° C. This period of time will generally suffice to drive off moisture from most samples, but occasional samples require a

longer time. After taking the dry weight it is well to replace the sample in the oven and subject it to a further drying of 15 minutes, weighing it again in order to verify the dry weight originally obtained.

49. Determination of Ash.—For the determination of ash, 15 grams of the ground leather should be burned in a platinum dish. The leather should be slowly heated until all volatile matter is driven off, then the charred mass may be broken up and the ignition concluded.

Mineral adulterations will be indicated by the analysis of the ash, and these are determined by a quantitative examination of the residue. Epsom salts are quite commonly used for brightening and tempering leather and also for adulteration, and if this material is the only constituent of the ash to be sought, its presence may be quickly determined by dissolving the ash in hydrochloric acid, precipitating iron and alumina with ammonia and filtering. After precipitating and filtering off the lime, the magnesium is determined in the cooled filtrate by precipitation with sodium-ammonium phosphate.

50. Determination of Oil.—To determine the oil and grease in leather, a 15-gram sample is extracted in a glass Soxhlet extractor for 3 hours, using about 100 cubic centimeters of petroleum ether as a solvent. The petroleum ether should be tested by evaporating 100 cubic centimeters in a tared dish and weighing any residue. The oil extraction should be conducted by heating the flask on a steam bath, so that there shall be a constant ebullition of the petroleum ether and a steady drip of the condensed vapor falling on the leather in the Soxhlet apparatus. When extraction is complete, pour the ether (which should now contain the oil and grease originally in the leather) into a tared, glass crystallizing dish, rinsing out the flask with a little additional petroleum ether. After evaporating the ether, the oil residue remaining in the crystallizing dish is dried and weighed. To determine the nature of the oils or greases used, a larger quantity of the leather must be extracted in order that the oil residue may be sufficiently large to admit of qualitative and quantitative examination.

liquors, which will give the leather a bright, clean shade. An illustration of the wide difference in union methods may be seen in the fact that in some union tanneries the first-layer liquors are as low as 8° Bk., while in others they run as high as 25° Bk. These liquors are, however, not of the same purity. The 8° liquor will show a higher proportion of tannin to the total solids than the 25° liquor, but, aside from this, the tannin strength of the 25° liquor is greater than that of 8° liquor. In tanneries where strong liquors are employed, considerable oak or chestnut-oak extract is used, the upper layers being strengthened, and the texture and color improved thereby.

71. Most of the union leather made is cropped; that is, the bellies and shanks are cut from the sides, making the product rectangular. The crop leather thus made commands a higher price than union side leather, because much waste is avoided when it is cut into soles The bellies, shanks, etc. are sold for scrap leather for inner soling, etc. A good quality of cut soles is made from union leather, and the method of selling these cut soles determines the method of tannage in some tanneries. A certain number of soles will be cut from several tannages of leather, and the leather that will give the largest number of soles to a given weight of leather is generally the best seller, if other considerations, as color, firmness, and texture, are equal. This causes tanners to endeavor to produce a light crop leather of a good color, strength, and closeness of texture. These qualities can be obtained by the use of very pure liquors of low barkometer degree. Since purity of the liquor is secured at the expense of leaching, it is really questionable whether this method of tanning pays. More leather can be made from a ton of bark by this process, but the actual gains will not be so great as when a heavy, well-filled leather is produced.

72. Green-salted hides are used for making union leather. They are well soaked, limed, unhaired, fleshed, and placed in clear water overnight, after which the hides go into the rockers. According to the method of tanning in use, the

rocker liquor and all other liquors vary in strength. After coming from the rockers, the leather is cropped in some tanneries, while in others it is tanned and finished as side leather and then cropped. When cropped out of the rockers, the heads and bellies are strung together and thrown on top of the regular leather in the lay-away vats. From the rockers, the sides go into the lay-away yard; from five to seven layers are given, using oak bark on every layer. The oak bark is ground fine, but not fine enough to prevent the circulation of liquor between the sides in the vats. After use in the lay-aways, the bark is sent to the leach house and leached with the hemlock bark for the union liquors. It is generally placed on the bottom of a leach, the hemlock bark being run in on top of it.

TABLE VII

LAYER SCHEDULE FOR UNION TANNING WITH COLD LIQUOR

Layer	Time in Layer Days	Strength of Liquor Degrees Barkometer	Approximate Percentage of Tannin
First	6	14	2.25
Second	10	16	2.50
Third	10	18	2.75
Fourth	12	20	3.25
Fifth	15	23	3.75
Sixth	25	25	4.50

73. A schedule of layers and liquors in a tannery using cold, weak liquors is shown in Table VII.

The leather from this tannery is of a very beautiful color, light in weight, and quickly tanned. The sapped liquors are strengthened by returning to the leach house, and no extract is used. The liquors are very pure; in fact, some of them are of such purity that 65 per cent. of the total solids are tannins. With this purity, the spent tan, of course, shows considerable tannin, the amount sometimes running as high as 2.25 per cent. The sides are completely tanned here and are

times with water at from 40° to 50° C., then transfer the mass of leather to a glass Soxhlet, and complete the extraction, uniting the extractives secured by the two methods. The boiling temperature necessitated by the Soxhlet extraction will cause the leather to run together and form a sticky mass, through which the extracting water can pass only with difficulty. This may be prevented to some degree by mixing the leather with several times its volume of sand before placing it in the extractor. For the water-soluble determination, 20 grams of the sample should be extracted, as just outlined, and the extractive solution brought to a liter in volume. This is then analyzed for tannins and non-tannins, according to the methods of tan-liquor analysis previously described.

53. Determination of Glucose.—Glucose in leather is determined in the water-soluble material by Fehling's solution after removing the tannin. The tannin is removed by basic lead-acetate solution, which is made as follows: 300 grams of lead acetate is mixed in a liter flask with 100 grams of litharge and 50 cubic centimeters of water. The flask is then heated on a boiling-water bath until the mixture is nearly white, more water being put in the flask to replace that which has evaporated. The mixture is then digested with 1 liter of cold water and filtered.

The lead-acetate solution having been made, 20 grams of the leather is digested with successive small portions of water, filtering after each digestion through a cotton plug stuck in the neck of a funnel. The temperature of the extracting water should be gradually increased from 40° C. for the first digestion to boiling water for the last two digestions. The extractive solution should amount to 500 cubic centimeters, and after cooling, 30 or more cubic centimeters of the basic lead-acetate solution is added, well mixed by shaking, allowed to stand for 15 minutes, and then filtered through a dry filter, collecting exactly 400 cubic centimeters. To the 400 cubic centimeters of filtrate add 30 cubic centimeters (or more if necessary to throw out the lead) of a strong magnesium-sulphate solution, shake, and filter on a dry filter. Boil

100 cubic centimeters of this filtrate with 3 cubic centimeters of strong hydrochloric acid for 3 hours, not allowing the volume to go below 75 cubic centimeters. This is for the purpose of inverting unconverted dextrin and intermediate products, which are generally present in commercial glucose and which, unless inverted, are not determined by Fehling's solution.

After boiling, make the solution slightly alkaline by the addition of a concentrated sodium-hydroxide solution; make up to 100 cubic centimeters and filter if necessary. Transfer the solution to a clean burette and use it to titrate 10 cubic centimeters of Fehling's solution. For this operation 5 cubic centimeters of each of the Fehling solutions are placed in a casserole, 40 cubic centimeters of water added, and the whole brought to a boil. Run in from 5 to 10 cubic centimeters of the sugar solution at a time, boiling the liquid 2 minutes between each addition, until the blue color has nearly disappeared. The sugar solution should then be added in smaller quantities and the time of boiling reduced to $\frac{1}{2}$ minute between each addition from the burette. The end point may be determined by the absence of blue color on looking through the supernatant liquor, or potassium ferrocyanide may be used as an indicator. If the indicator is used, take a few cubic centimeters of the solution, run through a very small filter, and add a little acetic acid and 1 drop of potassium-ferrocyanide solution.

54. It is well to make an approximate titration at first and then a second titration on another 10 cubic centimeters of Fehling's solution, adding nearly the whole of the required sugar solution at once, so that the time of boiling and titration is reduced to a minimum. Fehling's solution, of which 10 cubic centimeters equals .05 gram of glucose, is made in two parts as follows:

In making solution 1, dissolve 34.6 grams of pure crystallized copper sulphate in distilled water, then add 10 cubic centimeters normal sulphuric acid and make up the whole to 500 cubic centimeters.

In making solution 2, dissolve 125 grams of chemically pure potassium hydroxide and 173 grams of pure potassium sodium tartrate (Rochelle salts) in distilled water and make up to 500 cubic centimeters.

To make Fehling's solution, 5 cubic centimeters of each of these solutions are mixed just before using.

A convenient strength of the magnesium-sulphate solution is made by titrating 10 cubic centimeters of the basic lead-acetate solution with a strong solution of magnesium sulphate until no further precipitate is produced. One hundred times the quantity of sulphate solution needed for the titration is made up to a liter, and the use of this solution will result in the removal of the lead without a large residual excess of magnesium sulphate.

MANUFACTURE OF LEATHER

(PART 3)

LIMP, OR LIGHT, LEATHERS

PROCESS OF MANUFACTURE

1. Introduction.—In order to make a soft and pliable product known as *limp,* or *light,* leather, the hides or skins used require very much different treatment from that given to the hides in the manufacture of sole leather. The actual tanning for certain classes of leather is conducted along the same general lines as in the making of sole leather, but with weaker liquors and covering a shorter period of time. With these pliable leathers the tanning is really the smallest part of the manufacturing process, as the finishing of the leather requires a larger proportion of time and labor. The tanning, however, whether it be vegetable, mineral, or oil, must be suited to the use for which the leather is intended, as no amount of skilled finishing can entirely obliterate the defects of an improperly tanned hide. Because of the multiplication of operations in making light leathers, processes of manufacture differ to a greater extent than in the tanning process for heavy leather. Every light-leather tanner aims to attain the same result, but methods differ in each department of different tanneries; and nearly every tanner uses methods and formulas differing slightly from the methods and formulas of his competitors.

As they appear on the market, limp, or light, leathers

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

may have been made from whole hides or skins, or they may have been made by splitting heavy hides into a number of lighter pieces, or **splits**. The tannage of these hides, splits, or skins varies according to whether they are to be used for automobile leather, shoe leather, bag and strap leather, fancy leather, or glove leather. No general description can be given to include all classes, although some of the steps may be similar for the different grades.

In discussing light leathers each class will be taken up individually and, when possible to do so, reference will be made to like treatment in other branches of the industry.

As Part 1 deals entirely with heavy leather of vegetable tannage, we will first consider the light leathers which are also of vegetable tannage, and then follow with mineral and oil tannages.

AUTOMOBILE AND UPHOLSTERING LEATHERS

2. General Preparation.—In making leathers for automobile, carriage, and other upholstering purposes, the heaviest and most spready of green salted hides are used, in order to make one hide cover the greatest possible surface. Swiss and Paris hides are popular for such purposes, and hides from these sources are largely made into leather for this class of work. The hides are soaked, fleshed, limed in straight lime solutions, unhaired, and bated. (See Part 1.)

The bating of hides for automobile leather should be very complete, as the stock must be in as soft and open a condition as possible. Formerly manure bates were employed, but today either oropon, a material composed of ammonium chloride, wood fiber, and dry pancreas, or puerine is used. In using oropon, the paddle is about three-fourths filled with water at a temperature of 95° F. and about one-half of one per cent. of oropon on the weight of the stock is introduced. While the paddle is running, the hides are entered and the stock turned until all lime has been removed. The grain will

by this time have assumed a silky condition and the fiber is probably well separated.

In order to set the grain, secure a good, even color and obviate the danger from kiss spots. The stock is usually transferred from the bate to a spent tan liquor made acid with a small quantity of either an organic or a mineral acid.

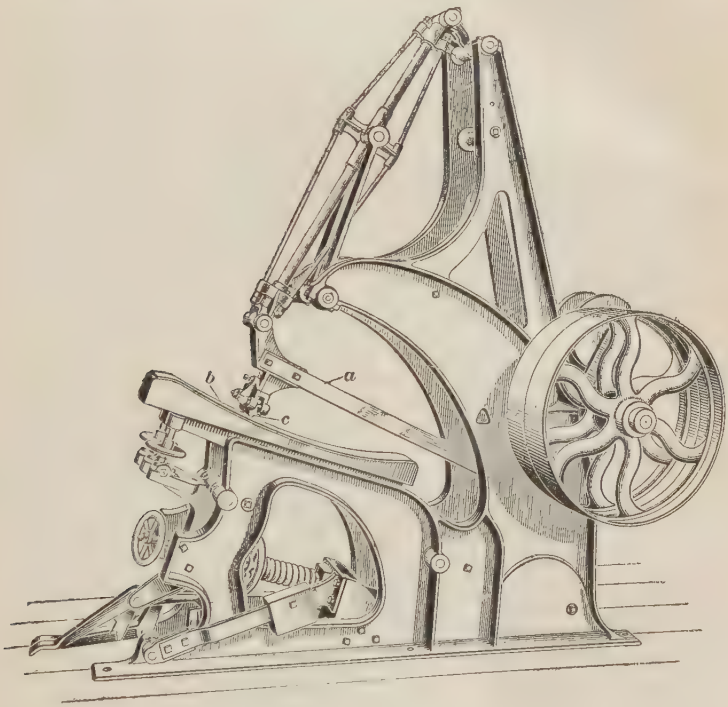


Fig. 1

When ready for tanning, the hides are hung by the butt on a rocker frame and rocked in the tan liquor. The hides go into the weakest liquor, the stronger liquor gradually working through the section of rockers until the leather receives the strongest liquor and is sufficiently tanned for the splitting machine. The tanning liquor is composed of a combination of two or more tanning agents, such as hemlock, oak, quebracho, gambier, and palmetto. When the leather is suffi

ciently tanned, the hide is run through a wringer, or piles of them are pressed in a hydraulic press, to remove the excess of tan liquor previous to splitting. They are worked on a stoning jack to remove wrinkles and to smooth out the surface.

3. Stoning Jack.—The **stoning jack,** shown in Fig. 1, is built of iron and is run by a side-belt drive. By means of a crank-shaft, an arm *a* supported and guided by a swinging truss is given a backward and forward motion, following the contour of an inclined metal bed *b,* the face of which is smooth and cut in the form of a segment of a circle. To the end of the arm is attached the *stone c,* which is a rectangular piece of metal with rounded corners and slightly longer than the width of the bed. When in operation, this tool is carried backwards and forwards over the bed at a distance from it regulated by the operator by means of a foot-lever. The leather is thrown on the face of the bed, under the moving arm, and the stone brought down on it. By the action of the stone the wrinkles and creases are removed, the leather being moved around under the stone by the operator, so that every part comes in contact with the stone, or smoothing tool. The grain side is finally split, the split being made light or heavy, according to the purpose for which the finished leather is to be used.

4. Splitting Machines.—Two general classes of **splitting machines** are in use, the *Union splitter* and the *belt-knife splitter.* The latter is the more popular machine and is found in most of the Eastern upper-leather tanneries.

In the **Union splitter,** the leather is presented to the edge of the splitting knife by gripping and drawing rollers. It is held on the rollers by carrying arms and is split by the power that rotates the roller by which the leather is carried.

The **belt-knife splitter,** shown in Fig. 2, effects the splitting by means of an endless belt knife *a,* against which the leather is carried by means of rolls. Machines of this type are not automatic, but require skilled labor to operate them economically.

After having taken off the grain split the remainder of the hide passes under the eye of the inspector, who decides the number and weights of succeeding splits. The grain splits are then retained in revolving tight drums with quebracho

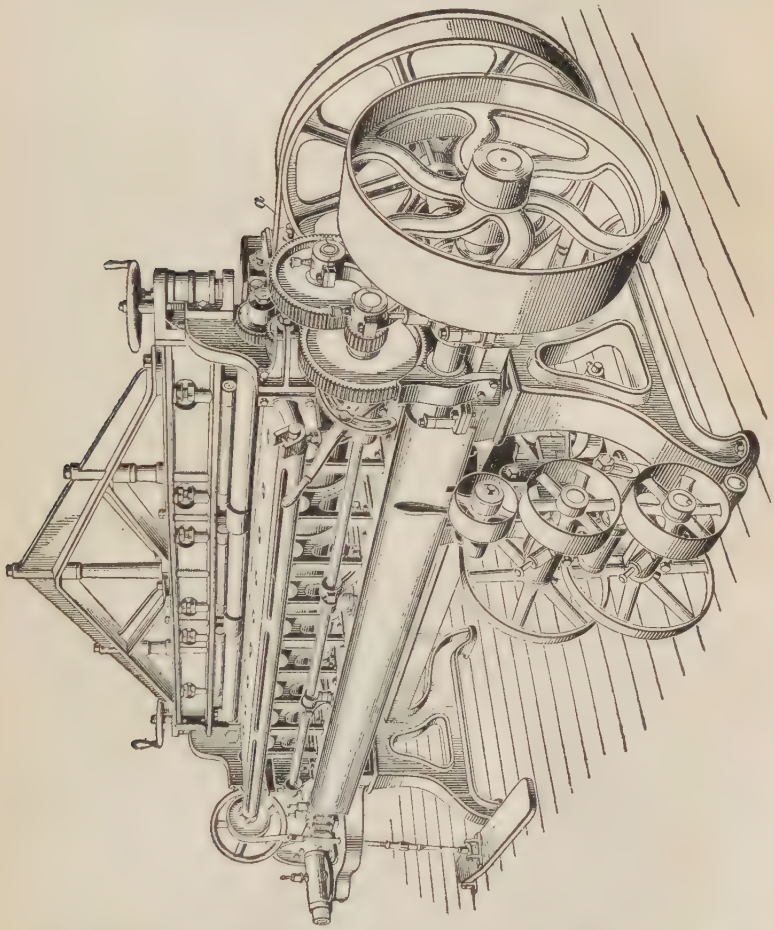


Fig. 2

and gambier liquors, the flesh splits being retanned in open vats, into which revolving paddle wheels dip.

After retanning, the splits are run into a wheel with sumac liquor, and after this treatment they are set out by hand or

by machine to remove the excess of water, and while on the table they are given a mixture of degras and cod oil. The leather is then closely tacked to heavy frames clamped in a stretching machine wherein the wet leather is stretched in all four directions. The frame is then tightly clamped to retain the stretch, and it is taken to the drying loft, where the leather dries, retaining the increased surface given it by the stretching. When dry, the splits are broken by hand or by machine to make them soft and pliable, and after buffing, if necessary, they are ready for an application of the coating. The grain splits are hand-buffed before being coated; machine buffing is also done by taking a very thin split from the grain.

5. Daubing.—The *daub,* or *coating,* for the leather is generally made by boiling down linseed oil with the desired pigment and thinning the mixture with naphtha. It is quite important that this daub should be properly made, and 2 days is generally required for the operation. The oil is boiled in a large kettle over a coke fire and constantly stirred. On the first day the temperature of the oil is run up to nearly 600° F. and then lowered to about 380° F. before it is left for the day. On the second day, the temperature is raised a little over 600° F., and the cooking is continued until the desired consistency is attained. The oil is gradually cooled, the fire extinguished, and naphtha added to thin the jelly-like residue; the naphtha is added in small portions with constant stirring. The highest grade of pigments that have been carefully ground in oil are thoroughly incorporated into the daub. All colors of coatings, different degrees of gloss, and varying thicknesses of the enamel are given to leather intended for different purposes.

The grains, splits, and buffings having been assorted and assigned to the different grades, weights, and classes of finished product, are stretched and tacked to frames and receive a heavy coat of the daub, which is carefully and evenly applied, the excess being removed. When the first coat has dried, a second coat is applied and the frames are placed horizontally in the drying oven, where the second coat is dried at a

temperature of about 120° F. When this second coat has dried, a thinner coat of the boiled oil is applied, and after this has dried, the surface is smoothed by rubbing with pumice stone. From four to eight coats of the bottom daub are applied, according to the requirements of the finished leather, and the drying may be done either in the air or in the oven, depending also on the future use of the leather. When the bottom coats have been applied and the surface smoothed, a coat of varnish and oil is applied and dried in the oven. This may be followed by smoothing and the application of a final coat of varnish and oil, and after drying in the oven, and a sun-and-air drying to remove the stickiness, the leather is taken from the frames, trimmed, and is then ready for the market. Some of the heavy leathers, as, for instance, the visors for military caps, are coated on two sides, each with a different color.

Various compositions other than boiled linseed oil are now being used for coating the leather, particularly for furniture, fancy embossed leathers and shoe leathers. Wood alcohol, amyl acetate, acetone, and other solvents are used as vehicles for carrying organic gums, pyroxylin, camphor, etc., in making up coats for shiny leather.

6. Furniture and ornamental leathers receive fewer coats than the heavier carriage dash and automobile leather, and they are given a grain either by boarding, by pebbling, or by the embossing press. The newer compositions for coating are frequently used on this leather.

The buffings, or grain splits from machine buffing, are very thin and are used for bookbinding and for covering boxes, etc. They are coated, colored, and surfaced and may be embossed.

The popular so-called *Spanish leather* that is now frequently used in upholstering for mission furniture is made by tanning the hides in strong quebracho liquor, which draws the grain and gives the leather its unique appearance. In finishing, it is dyed to the desired shade and coated so that the pigment fills the wrinkles in the surface and accentuates the irregular

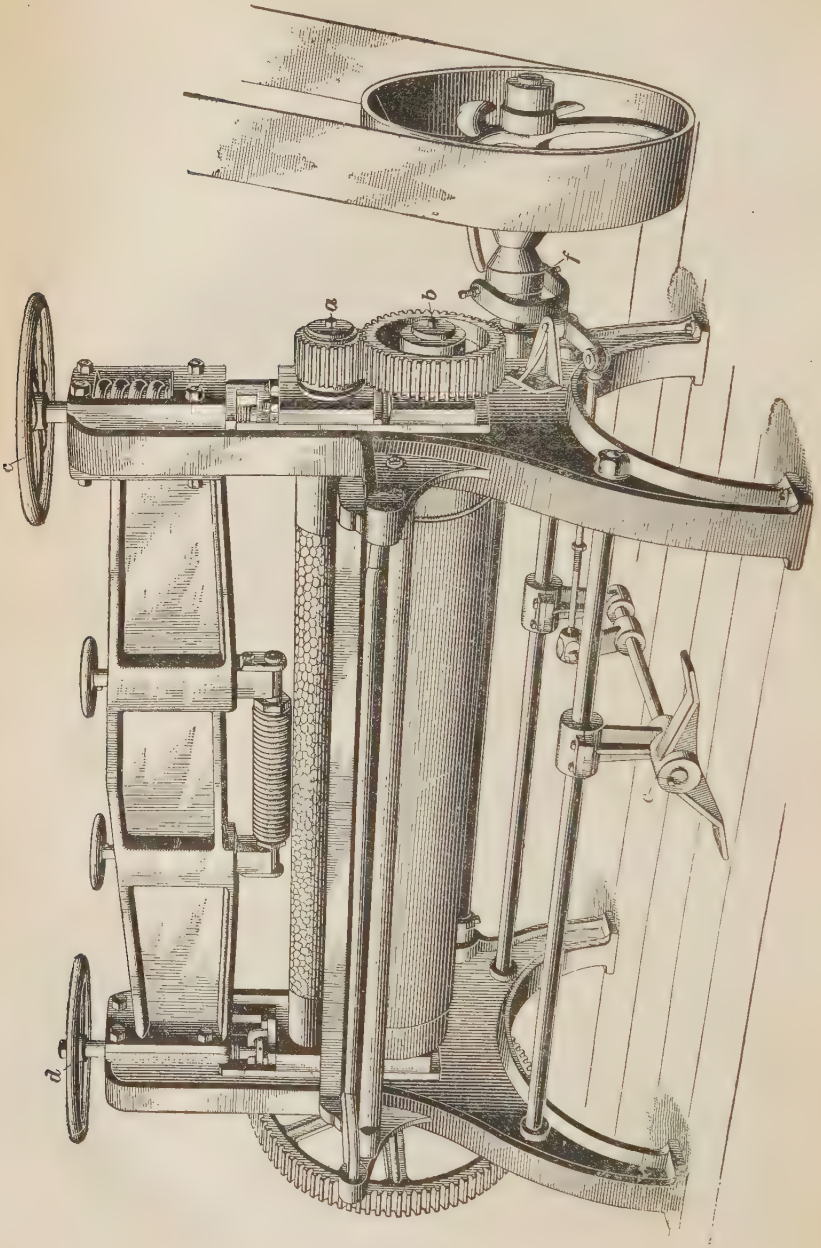


FIG. 3

grain. Spanish leather is also made by embossing the leather and then staining.

7. Embossing.—For embossing, a heavy pressure, distributed over a large area of leather, is needed. The embossing machine shown in Fig. 3 consists of two geared rolls *a* and *b*. The lower one *b* is smooth and forms a supporting surface for the leather that is to be embossed. The upper one *a* is smaller, and the design to be embossed is cut in its surface. The leather is fed between the moving rolls and receives the design from the upper roll. The pressure is regulated by hand wheels *c* and *d* at either end of the machine, and a foot-treadle *e*, connected with clutch *f* on the drive shaft, assures perfect control of the machine by the operator.

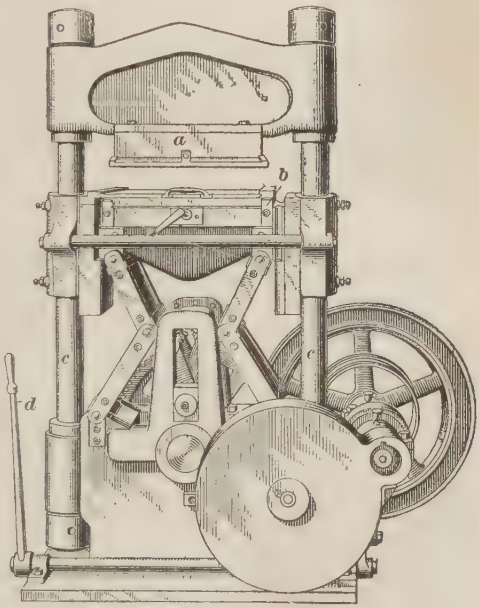


Fig. 4

8. A large proportion of the graining and embossing of leather is done by embossing presses similar to the machine illustrated in Fig. 4. A plate in which the pattern of grain or embossing desired on the leather has been cut is attached to and covers the bottom of the heated head *a*. The leather is laid on the bed *b*, and the lever *d* sets in motion the gears that raise the bed along the guide rods *c* until the leather comes in contact with the embossing plate on the head. The leather is subjected to enormous pressure, giving it the impression

of the particular pattern on the plate. The bed is then automatically lowered, and another portion of the leather is moved on the bed to receive the pattern. The head may be heated by gas, steam, or electricity.

BAG, CASE, AND STRAP LEATHER

9. Vegetable-tanned leather for bags and straps is made from green salted hides. The hides are soaked and split into sides after coming from the soaks. They are then limed, unhaired, fleshed, and bated. After bating, the sides are attached to sticks and go into the rockers. The rocker liquors contain sufficient fermentative acids to neutralize any lime not removed by the bate, and to plump the sides. The small amount of tannin present serves to color the stock and prepare it for the subsequent tan liquors. After the rocker treatment, the hides are moved to the weakest of a series of vats containing progressively stronger liquors. The hides are moved forwards throughout the series until the strongest vat is reached. After hanging in the last vat the required length of time, the tanning is completed to the required degree. The time required for the tanning varies in different yards, being as low as 15 days in some and as high as 30 days in others. As the sides are to be split, complete tanning is not necessary, but it is essential that the sides should be colored entirely through, so that the splitting knife will have a homogeneous substance on which to work. The liquors are made by combining hemlock and oak barks, myrobalans, chestnut, and quebracho extracts in proportions determined by cost, character of leather desired, and the ideas of the tanner.

10. After tanning, the sides are taken to the wringer and the excess of moisture removed. They are then smoothed out on the stoning jack, when they are ready for the splitting machine. After splitting into as many splits as the thickness of the side allows, or as the desired weight of the leather which is being made, requires, the splits are trimmed by hand and may be taken to the shaving machine for smoothing and

to remove any humps. The splits are then retanned in a revolving drum, or wheel, with extract liquor. Some of the liquors which are in common use for this purpose are quebracho, cutch, gambier, and palmetto extracts. The wheel treatment requires from ½ to 2 hours. From the retanning wheel, the splits are carefully spread out and piled, the piles when completed being covered with canvas and allowed to stand from 24 to 48 hours, so that the liquor received in the wheel may complete its combination with the hide substance.

After retanning, the leather is *cleared* by being run in a revolving drum, first with water, then with a solution of borax, then water, then a weak solution of sulphuric acid, and finally with another water, each solution being removed before the next solution is added. After clearing, the splits are run in a wheel with a sumac liquor, and occasionally some of the oiling is done in this wheel. The leather is then sorted and different grades assigned for different colors and for different purposes. The grain splits showing no hide imperfections are finished in the natural color for the best grades of leather. When the grading is finished, each lot of leather is dyed the assigned color, the dyeing being done either in a vat with a paddle wheel or in a tight drum. Leather to be dyed on one side only is, of course, colored by hand or by the blackening machine.

11. After dyeing, the leather is hung over sticks to harden, or it may be worked out and the excess of moisture removed by the machine. When properly tempered, the leather is worked and oiled by hand on a table. The table is swabbed with oil, the split being laid on it grain side up. After working out the excess of water and breaking or softening the leather, the grain is lightly swabbed with oil and then tacked on the drying frames and dried. When dry, it is removed from the frames, moistened to the proper degree, and a light oiling or a seasoning applied. The leather is then thrown over wooden horses and allowed to temper, and may receive subsequent treatments with either seasonings alone or seasonings containing dyes, to bring the color to the desired

shade. After the seasoning treatment is completed, and when properly dried, the leather is surfaced on a surfacing machine, and may be finished with a glassing machine. It is then *boarded* by hand to break the leather, complete and make permanent its limp character, and give it a particular style of grain, if desired. This is done by light pressure on the cork-faced boarding tool strapped to the arm of the operator, the leather being doubled and the tool moving over the fold of the leather. Different degrees of dampness and different ways of operating the board result in different grain surfaces.

12. If the leather is to be embossed in imitation of any grain desired, the embossing is done before or after the machine surfacing. The leather should be properly dampened, and, after embossing, it is dried and boarded. If the leather is to be blacked, the blacking is applied after seasoning. Three coats of any amyl acetate black are given, one coat being allowed to dry before the next is applied.

It may be finished smooth or may be dampened and embossed in imitation of seal, or any desired grain, after which it may be run through a splitting machine to produce the particularly light leathers used for card cases, for covering boxes, or for decorative purposes, etc.

The grain split from the hide is made up into the better grades of bag, strap, and fancy leather, while the flesh splits are generally used for cheap bag and strap leather, rough gloves, and innersoling. The flesh splits are frequently dyed, finished, and embossed, and sold for grain leather.

13. For certain kinds of strap leathers, also harness and belting leathers, where strength is the principal requisite and a slight darkening of the color is not objectionable, it is customary to fill the leather with a large amount of oil, the amount of oil and grease introduced often running as high as 45 per cent. of the weight of the finished leather. The material and processes employed are as follows:

14. Stuffing Materials.—The treatment of leather in such a manner that it will contain an amount of grease or oil

such as its future use may require is called *stuffing*. Stuffing is done both by hand and by machine, largely by the latter method. The former is used only on certain classes of leather.

For stuffing leather, the oil par excellence is cod-liver oil. It has been in use since the early days of the industry, and as yet no other oil has been found that can satisfactorily displace it. Cod-liver oil has a good body and remains in practically the same state in which it entered, thus giving to the leather a permanent mellow feeling.

This oil is expensive, and therefore substitutions are common. Seal, menhaden, and mineral oils are commonly used for this purpose.

It is almost impossible, with any marked degree of certainty, to detect the fish oil when mixed with cod-liver oil. Fish oils have more gum than the genuine cod-liver oil; but cod-liver oil and menhaden oil have the same color and gravity, and their range of odor and taste is about the same.

Menhaden oil, when cold pressed to remove the foots, is a good substitute for the average grade of cod-liver oil.

Stearin, tallow, beeswax, Japan wax, and paraffin wax are all used for stuffing certain kinds of leather.

Heavy refined mineral oils are largely used for mixing with cod and fish oils for stuffing heavy leather.

Neatsfoot oil is used with satisfaction if a good cold-tested oil is secured; otherwise, a cold temperature will congeal the oil and thus turn the skin white.

Sod oil is largely used for stuffing. It is pressed out from skins, and is ready for use after boiling and undergoing clarifying treatment.

Degras is the oil obtained from wool during its cleansing process. French degras is the surplus oil obtained in the manufacture of chamois leather. It is frequently adulterated and is put on the market in all grades.

Glycerine is used by some tanners instead of degras. It imparts to the leather a high degree of softness, but it should not be used alone, as it possesses a corrosive action and, being

soluble in water, is easily removed from the leather by dampness.

Porpoise oil is much valued for stuffing.

Wool fat, obtained from the solvents used after extracting wool, is sometimes used as a substitute for degras.

Olive oil is used in leather dressing, particularly in alum tannage.

Castor oil is largely used, especially in its sulphonated form, known as Turkey-red oil, which is made by treating cooled castor oil with successive small portions of strong sulphuric acid. After standing, the oil is separated with salt solution and carefully neutralized.

Sperm oil is occasionally used in finishing leather, and it is sometimes used in fat liquors.

The yolks of eggs are used in stuffing high-grade glove leather, as it contains about 30 per cent. of an oil known as egg oil.

15. Hand Stuffing.—In hand stuffing, the leather must be in a damp condition and the daubing mixture consisting usually of cod-liver oil and tallow, is applied to the flesh. By means of a heavy slicker, the hides are worked on the table and then placed in piles in a warm room. The operation is repeated several times or until the necessary amount of oil has been introduced. As practiced, the operation of hand stuffing consists of rolling the sides into bundles, with the grain side in, and softening by heating; then the warm oil and tallow is applied with a brush to the flesh side.

16. Drum Stuffing.—In the drum-stuffing method, the stuffing is effected by placing the hides and stuffing material in a revolving drum *a*, Fig. 5. The hides are dampened thoroughly on both sides and allowed to lie in a pile, which is then covered with damp cloths. The drum is heated by steam or hot air for some time before receiving the stock. The heat is turned off and the hides placed in the drum, which is then run for some time with the door loosely closed. This operation loosens up the goods and regulates the temperature. The stuffing material is then run in hot, but not hot enough

to scald the hides. The tight door is put on the drum and the stock wheeled for from ½ to 1 hour. The drum is stopped and the door opened, and the drum is then slowly revolved for a few minutes. The hides are finally taken out, smoothed, and laid in piles.

They are generally stoned as soon as possible on marble or plate-glass tables (it is best to stone on the grain side first) and then hung up until nearly dry. The operation is repeated on the flesh side, removing all marks of the stone, after which the sides are again hung up until quite dry. There

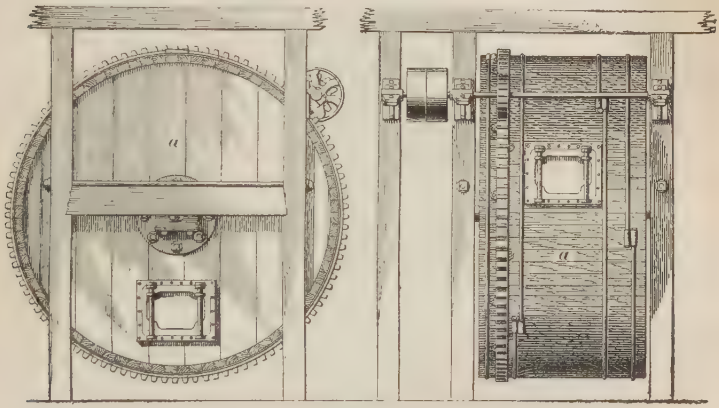


Fig. 5

are several patented forms of stuffing drums in which the heating is effected by means of coils containing steam or hot air. The coils keep up the temperature of the drum while the stuffing is going on and do away with the water of condensation.

A *hot-air stuffing mill* is shown in Fig. 6. The air for the drum *a* is heated by steam coils in the heater *b*, from which the heated air is forced into the stuffing drum by means of a small fan blower, as indicated.

17. Fat-Liquoring.—For certain kinds of vegetable-tanned leather, especially light leather, the oil and greases are replaced by so-called fat liquors. These fat liquors are simply emulsions of different oils, fats, and soaps, the character of

which depends on the kind of leather and its future use. Egg yolk is an example of a natural fat liquor. For some leathers, a fat liquor made up of water, olive-oil soap, olive oil, degras, and Turkey-red oil, is used. Some tanners use a mixture of water, neatsfoot oil, glycerine, and castor-oil soap, and there are many other combinations of soaps and

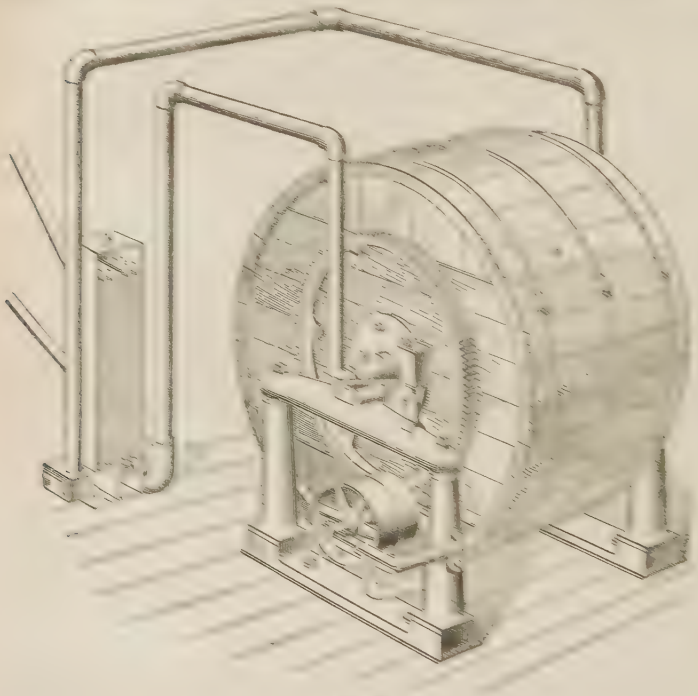


Fig. 5

oils used for fat liquors. The preparation and use of fat liquors is a part of the finishing process that has a marked influence on the softness and durability of the leather produced. Fat liquoring is done in a rapidly revolving drum, and the fat liquor added continuously during the revolution of the drum.

18. Buffing, or Whitening.—The buffing, or whitening, required in the manufacture of some classes of leather

cylinder, is lowered by means of a foot-treadle until it comes in contact with the leather. The pressure of the tool on the leather is regulated by the operator, who keeps the leather moving so that one section of the surface does not receive more of the abrasive action of the cylinder than another.

The whitening machine illustrated is made of iron. The rotary cylinder, or whitening tool, *a* is driven by belts at either side and running on a small countershaft fixed in boxes at the end of the supporting double truss, or pendulum, *d*. The belt running the countershaft passes between the parts of the truss and over a pulley at its upper end, and thence to the main driving belt. The pitman *e* is connected with the balance wheel *f*, and from it receives a backward and forward motion. The foot-treadle *b* is for regulating the distance between the cylinder and bedplate *c*, and, accordingly, the pressure on the leather. The bedplate is of polished brass, is slightly wider than the cylinder, and is inclined. A revolving emery wheel *g* travels constantly from one edge of the revolving cylinder to the other, keeping sharp the faces of the knives, or spines of the cylinder.

SIDE LEATHERS

20. Splits.—Leathers made from split cow and steer hides tanned by a vegetable-tanning process are used to a large extent in various grades of shoes. The same conditions as to varieties exist with this class of leather as with other classes. The hides are usually split out of the lime, the grain going into mineral tannage while the split is vegetable-tanned. This flesh-split is used largely for cheap shoes as brogan leathers, are stuffed in the drum and then grained or waxed as desired.

The splits from side leathers are also sometimes given a pyroxylin finish and are known as *dope splits*.

When the splits are to be finished for cheap shoe leather the stock after stuffing is cleaned smooth by working on the whitening machine after which it is ready for the color.

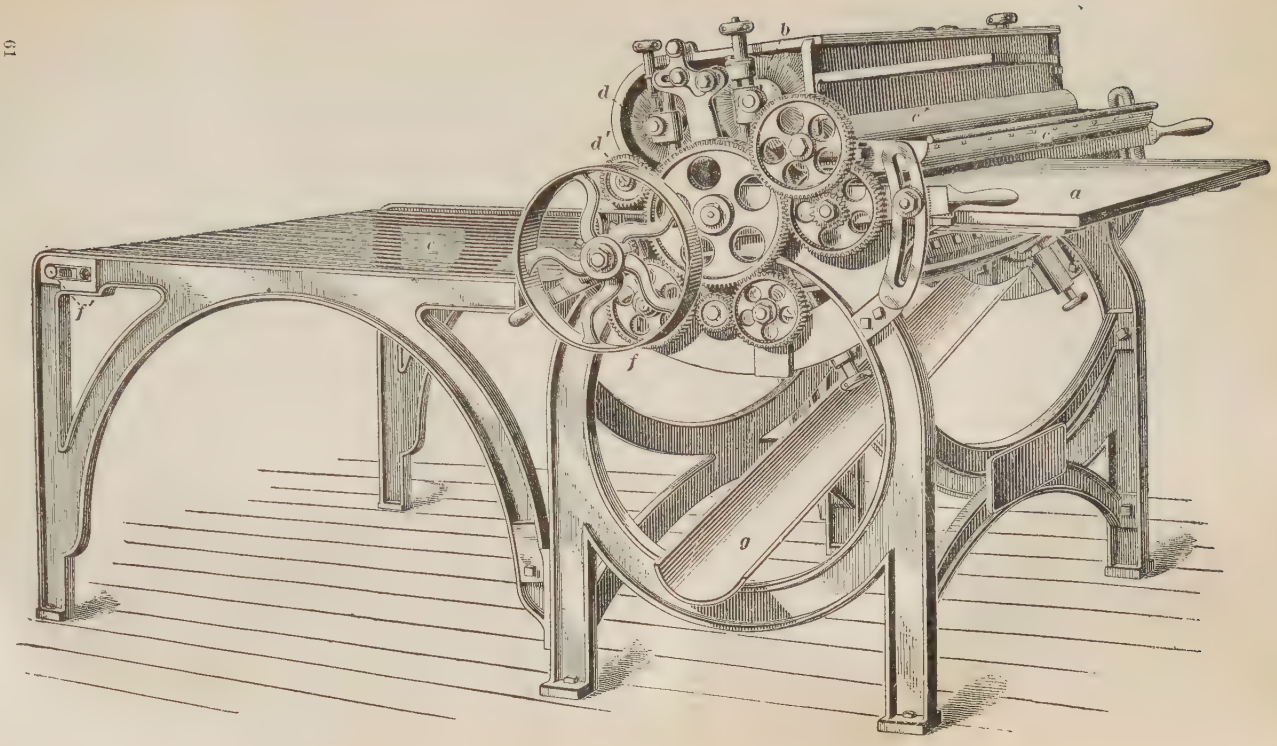


Fig. 8

21. Blackening.—After whitening, or buffing, the leather is ready for blackening. For the heavy grades of upper leather, this operation is preferably done by hand. The liquid blacking or other dressing to be applied to the surface of the leather is spread evenly over the hide by means of oval brushes made of fine bristles. The excess of blacking is removed by other brushes, care being taken that no blacking reaches the under side of the leather.

22. Blackening Machine.—A popular machine for blackening leather is the *Batchelder,* shown in Fig. 8, or modifications of it. In this machine, the leather is spread on the table *a* and fed into the machine. The edge of the leather is engaged between the surfaces of two rolls and then passed over a third roll, which forms a supporting bed for the skin, while the brush *b* applies the blacking. The blacking or other dressing is in the receptacle *c,* and the fluted roll *c′* running at the edge of the blacking receptacle supplies the brush with the coloring matter. The brush *d* seems to work the blacking into the leather and also to remove any excess. After passing under the second brush over the supporting roll *d′*, the leather is delivered to a moving bed *e*, formed by endless tapes extended around rollers *f* and *f′* and driven by gears.

As the hide does not always cover the roll supporting it under the blacking brush, some blacking reaches the roll. This roll must be kept clean, otherwise the under surface of a wide portion of hide will become soiled with the blacking. A wiper or cleaner of some flexible material, held by an adjustable bar against the lower surface of the roll, effects the cleaning. The material wiped or scraped from the roll drops into the trough *g* and passes to a bucket provided for that purpose.

The rows of bristles on the brush are so arranged that alternate rows incline in different directions, those of one row inclining toward one end of the cylinder and those of the next alternate row toward the opposite end. In this way, the ends of the bristles, besides traveling over the leather in

the direction of rotation of the brush roller, also, when in contact with the leather, spring in opposite directions longitudinally and thus work the blacking backwards and forwards, as well as in the direction of the movement of the roller, effectually blackening the leather and preventing streaking.

If the leather is to be dyed, the dyeing may take place immediately before or after the stuffing, and in some processes the dye solution is added in the stuffing drum.

SHOE, GLOVE, AND FANCY LEATHER

23. In the manufacture of the shoe leather, as well as glove and fancy leather, there are certain mechanical processes which must be followed in order to obtain the desired results. As these operations are common to all three of the classes mentioned, it will be well to give a description of them here.

24. Working Out Skins.—For *working out* the skins in different stages of some processes in light-leather tanning, the serial table machine shown in Fig. 9 is largely used. Machines of this type are used also for unhairing light skins, but they are used mostly for working out and for setting out the skins. Through treatment by this type of machine, most of the water is removed from the skin, the grain is made fine and silky, and the skin is well stretched and left in good condition for oiling and drying.

The rubber-bolstered tables a, a_1, and a_2 are attached to the endless chains b, and are slowly carried between the double rolls shown at c and c_1. The rolls are spirally bladed, and the skins, being carried between the rapidly revolving rolls, are subjected to their action both at c and at c_1. As the machine is constantly in motion, the skin is thrown over table a with its backbone lying along the upper edge. The table is then carried up and passes between the rolls at c_1. When the table is clear of these rolls, the bolsters and skin are automatically moved so that the backbone, which was not worked between the first pair of rolls, is brought in position to be worked by the second pair of rolls at c. In addition

to setting out the backbone, the upper rolls perform a second working operation on the other parts of the skin. The bolster

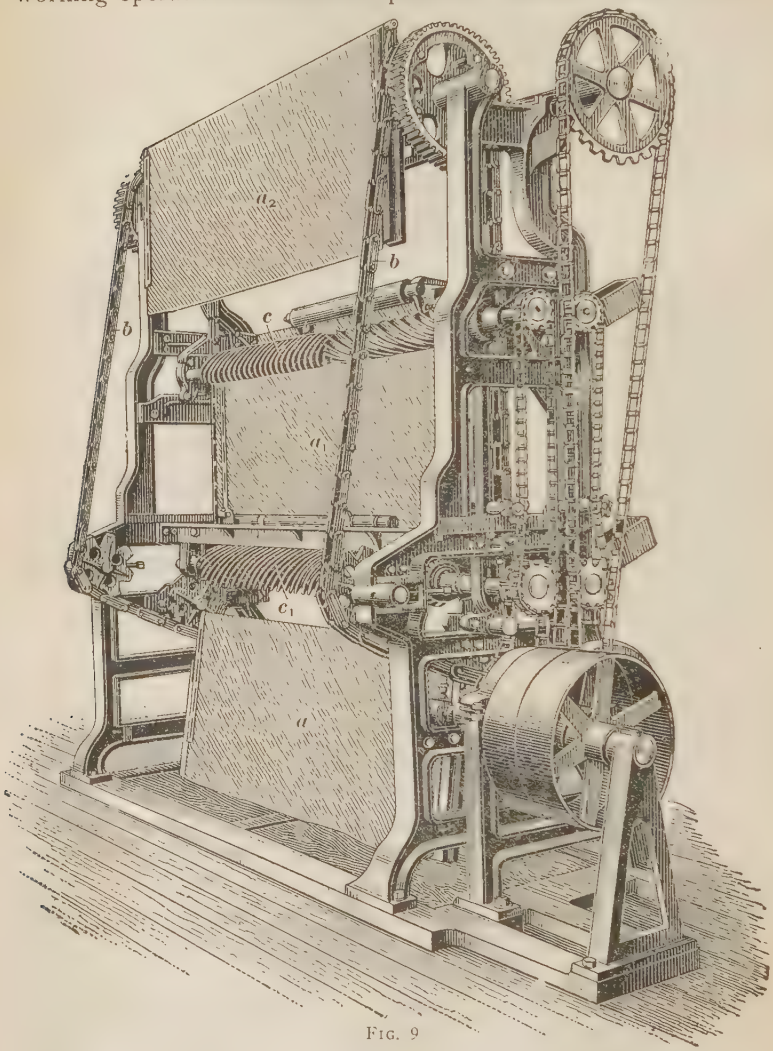


Fig. 9

is now moved back to its original position and the table descends. The skin is then removed, another skin thrown on the table, and the operation repeated indefinitely.

The wet skins are put on the tables at one side of the machine and the worked skins are removed at the other side, so that each operator has the one duty to perform. Recently patented inventions provide for the automatic removal of the worked skin, so that only one operator is needed for each machine.

25. Shaving.—After tanning the stock, it is piled on horses for a short time to drain free from excess moisture and is sometimes pressed and then milled for half an hour

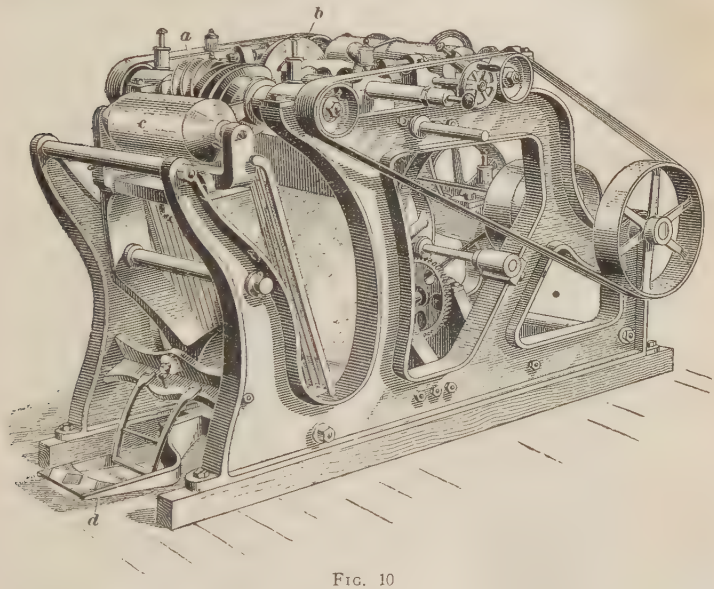


Fig. 10

with flour or talc. The skin or sides are then shaved on the flesh to make them smooth and to remove any lumps or irregularities in thickness. This work was formerly done by hand, but is now almost universally accomplished on the shaving machine shown in Fig. 10. The machine consists of a cylinder *a*, having spiral blades set in its surface. The blades are ground by the emery wheel *b*, which moves from one end of the shaving cylinder to the other while constantly revolving. The machine being set in motion by a belt shifter, the

skin is thrown over the roll *c*, and pressure on the foot-treadle *d* throws the roll *c* forwards, bringing the skin in contact with the rapidly revolving shaving roll *a*. The skin is moved by the operator so that, by varying the pressure of the skin against the shaving roll, any desired amount of shaving may be done on any portion of the skin. The spines of the shaving roll are constantly being sharpened by the action of the grinding wheel *b*.

26. Staking.—After light leathers are dried, it is necessary to soften and loosen the fibers so that the leather becomes soft and pliable. This operation is called *staking*, and was formerly done entirely by hand, the workmen pulling and

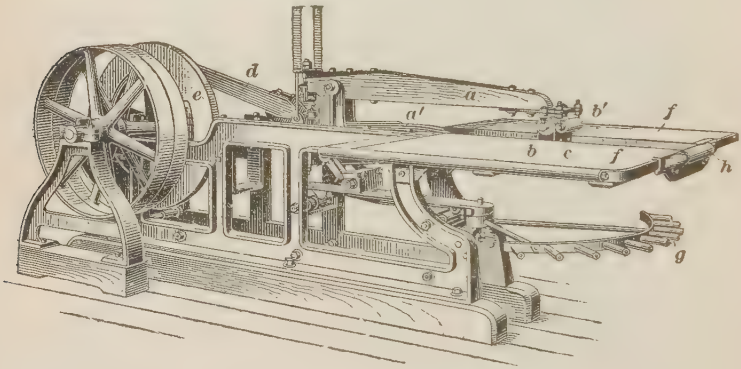


Fig. 11

stretching the skins across a stake, or perch, and using hands and knees in the laborious task. In Fig. 11 is shown a representative type of staking machine by which the greater part of the staking is done, machine staking having largely superseded the hand method.

The machine consists of a pair of tongs *a* and *a′*, the upper arm *a* having at its extremity two felt-covered rolls *b* and *b′*, between which enters the staking blade *c*, attached to the extremity of the lower arm *a′*. By means of a crank and a connecting-rod *d* the tongs are attached to the crank-wheel *e*, causing the tongs to move backwards and forwards in the

divided table *f*. A cam actuated by the connecting-rod opens the jaws of the tongs on the forward stroke, and they are closed by springs on the backward stroke. The knee pressure regulator *g* adjusts the pressure of the staking tools on the jaws, so that any desired pull on the leather is at the control of the operator.

In staking, one end of the skin is laid against the roll *h* and held by the pressure of the operator's body, the sides of the skin being firmly grasped by the hands and inserted between the staking jaws of the tongs. The skin is moved about so that all parts are subjected to the action of the staking tools, the pressure or pull necessary for any particular skin, or for any particular part of a skin, being regulated by the lateral movement of the operator's knee against the pressure regulator *g*.

27. Seasonings.—The finishing solutions applied to the surface of light leathers are known as *seasonings*. In addition to giving the finished appearance required by the market, they serve as a basis for a glaze and make the grain surface more elastic. Their composition varies with the class of leather being finished, and many materials and combinations are used in making the seasoning. For colored leather, a mixture of egg albumen, flax seed liquor, and gum tragacanth is frequently used, and in addition the solution may contain some of the dye originally used on the leather. Blood, casein, and milk are also used in seasonings for this class of leather. Seasonings for black leathers, in addition to the materials mentioned, often contain dichromate of soda, logwood liquor, isinglass, Irish moss, etc. Skivers and thin skins are often treated to seasonings of gums and resins dissolved in alcohol.

The composition of seasonings is really a matter of experience, to be determined by the currier who has watched the effects produced by different ingredients and different proportions of the same ingredients. Each currier has his own formulas for different effects, and probably no two agree on the question of seasonings, except that the seasoning should be applied in very light coats and should be well rubbed into the leather.

28. Surfacing.—After being properly prepared, the leather is submitted to a surfacing process. The surfacing operation is sometimes performed by hand, but by far the greater part of the leather finished in the United States is *glazed, rolled,* or *pebbled* by machinery. The operation of the surfacing machine shown in Fig. 12 is similar to that of the rolling machine used in the manufacture of sole leather, but it is lighter in construction. The roller *a* runs in boxes on the end of a beam *b* connected directly to a wheel *c* on the drive shaft, which imparts a direct backward and forward motion to the beam. The end of the beam is supported by a pivoted truss *d,* which also serves as a guide, so that the

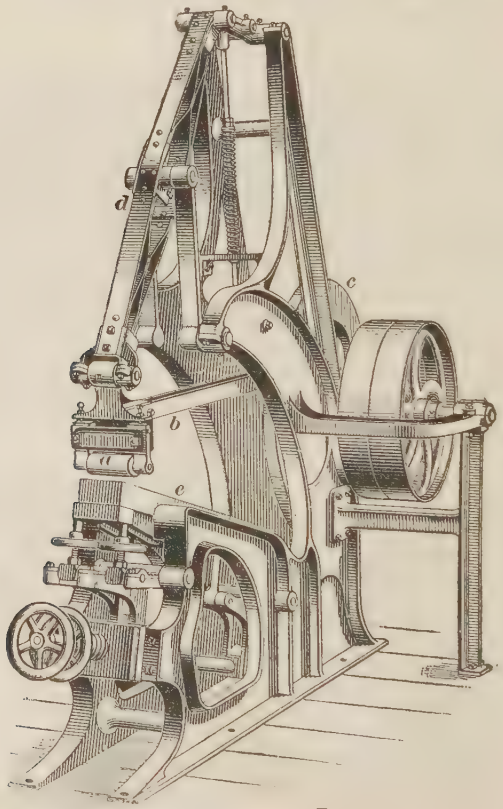


FIG. 12

roller runs in a line parallel to the face of the bedplate *e*. The bed on which the leather is laid is inclined and its face is straight. On all machines for finishing the surface of leather, every precaution is taken to guard against oil or grease coming in contact with the leather. A single grease spot will greatly depreciate the market value of a skin. The rolls are generally self-oiling and the boxes are especially devised to guard against oil leakage.

29. Glazing.—For *glazing,* a smooth roller is used, the leather being laid on the bed and moved around under the moving roll, so that every part of the surface receives its polishing action. The heat essential to a good polish, or glaze, is supplied by friction of the roll, and the operator must be careful not to maintain too great a pressure on the leather, or the heat generated will burn the leather. The bed is controlled by screws in front of the machine. One screw raises or lowers both ends of the bed at the same time, another screw regulates the pressure for both ends, and the other screws adjust the bed to any desired position.

For the final finishing, a machine in which a piece of smooth, rounded glass is substituted for the roll *a,* Fig. 12, gives the leather a high luster.

An electrically heated roll that has lately appeared on the market has become quite popular. The roller is heated to the temperature necessary for a good polish, so that pressure need not be resorted to in order to produce heat.

30. Pebbling.—For *pebbling, dicing, graining,* or for giving the leather any desired surface, different rolls are substituted for the smooth roll used for rolling and glazing. These rolls have their surfaces cut in the desired figure, and by the action of the machine the design is imparted to the surface of the leather.

VEGETABLE-TANNED CALFSKINS

31. Black and colored shoe leathers made from calfskins by a vegetable tannage are manufactured in the following manner: The skins are soaked, fleshed, and then limed in a

mixture of lime and red arsenic, or one consisting of lime and sodium sulphide. After removing the hair, the skins are bated in oropon, or by means of bran or organic acids. After washing off the bate, the tanning of the skins begins. Various liquors are used in different tanneries, and they are generally combinations of two or more tanning agents. Among the materials used are hemlock, oak, quebracho, palmetto, and gambier The tanning is done either by hanging the skins on rockers in the liquors or by the use of a paddle wheel. The same general rules for vegetable tanning of heavy leather, as to gradual increasing strengths of liquors, are observed, but the tanning is conducted with weaker liquors and in such a manner as to produce a tough, mellow leather.

32. After the tanning, the heavier skins may be split and the splits retanned in a paddle wheel with either gambier or quebracho liquor. The lighter skins are immediately drained, pressed, shaved, and they are then ready for stuffing. The stuffing is sometimes done with oils, but more often a fat liquor made of soap and degras, or soap, oil, and degras, is used. After the stuffing, the skins are set out by hand or machine, and then dried. The finishing is done by dampening the dried skins and then running them in a wheel with sumac liquor, so as to prepare them for the coloring. If a natural or a lighter color is desired, the skins are sometimes cleared by running in the mill first with borax water, following this with an acid solution, and finally washing with pure water, after which they are set out by hand or by machine. For coloring, the skins are first drummed with a fustic-extract solution, and after draining off the extract liquor, the dye solution is added to the drum and the drumming continued until the coloring is complete. To set the color, the skins are then rinsed in a weak solution of alum or other chemical, depending on the character of the dye used, and they are then set out. When dry, they are slightly dampened in sawdust and made soft and pliable by staking on the machine or by hand. Then they receive a coat of paste made up of flour and tallow, and when this is dry the skins are lightly glazed.

The seasoning is applied and the skins are glazed and hung to dry. After this, another coat of seasoning is applied, followed by a glazing. The stock then receives any desired graining, and the leather is ready for market.

33. If black leather with a purple or yellow flesh side is desired, the flesh dye is put in the drum, and the grain dye is applied by machine, on tables by hand, or by folding the flesh side together and immersing the folded skin in the dye. On vegetable-tanned leather, the black coloring is generally effected by a solution of logwood and soda, followed by a striker solution made of a soluble iron salt. After the grain is dyed, it is washed off with warm water, set out, and a light coat of oil given. The leather is then hung up to dry.

The numerous brands and varieties of vegetable calf leather now on the market are produced by varying the finishing treatment of tanned calfskins as regards the amount and character of stuffing, the character of pastes and seasonings, and the luster and style of grain given the leather. The general treatment for all these leathers is as described. However, no two factories tan or finish leather by exactly the same methods.

34. Wax Calf.—The class of leather known as *wax calf* has lost its popularity, and hence is not so extensively made as formerly. This leather is made from calfskins by a vegetable tannage, and is very heavily stuffed with oil, grease, and wax. The flesh side is shaved and carefully smoothed by hand, and grease black is applied to this side, the grain side being left uncolored except for the color of the tanning agent used. The finishing is done on the flesh side, and the entire skin receives a final oil soaking and is then rubbed to give it a final market finish. The grain side being next the foot of the wearer of the shoe, the flesh side of the leather is exposed to wear, and scratches or scuffs received are easily concealed by an application of shoe polish. Because of the stuffing used in this class of leather, the clothing is easily soiled on coming in contact with the shoe, and this has helped to decrease the popularity of this wear-resisting leather.

During the World War the leather used for army shoes was finished on the flesh in somewhat the same manner as described. No coloring material, however, was used and so the shoes had the natural color of the tanned product. Such leather was used only for heavy service, and a leather finished on the grain was furnished for shoes intended for ordinary street wear.

VEGETABLE-TANNED SHEEPSKINS

35. Sheepskins come to the tanner salted, either as they are taken from the animal or with the wool removed, the skin having been pickled in sulphuric acid and salt solution. Large quantities of skins are split and the pickled splits are shipped to the tanners in casks.

Sheepskins are made into a variety of leathers and are tanned by processes similar to those used for tanning other skins. Considerable sheep leather finds its way into the uppers of shoes supposed to have glazed-kid uppers, and sheep leather is largely substituted for kid and goat leather for other uses. The whole skins are tanned by the oiling process, the chrome process, the vegetable process, or by a combination of mineral and vegetable tannages, the leather being used for shoes, coats, aprons, suspenders, bookbindings, linings, etc. When the sheepskins are split, the grain split or skiver is generally tanned by vegetable processes for linings, sweatbands for hats, bookbindings, gloves, etc. The flesh splits, or fleshers, are used for making chamois leather.

36. Preparation of the Skins.—The wool is removed from the sheepskin by thoroughly washing the skin first and then lightly painting the flesh side with a mixture of lime and sulphide of sodium. The skin is then folded along the spine line, flesh side in, and piled in low piles to stand until the wool slips easily. After the wool is pulled, the skins are washed in clean water and put into the limes. After liming, the skins are fleshed, washed, and bated, or drenched, in organic acids or bran. They are then washed and placed in a pickling solution made of salt and sulphuric acid. When the

pickling is complete, the skins are removed, allowed to drain, or are pressed, and are then ready for shipment to the tanner. If skivers, or splits, are to be made, the skins are split by a belt-knife machine on coming from the limes. The pickling of the skins preserves them and also taws the skins into a kind of white leather.

Sheepskins are very greasy, and, to get the best tanning results, the grease must be removed. Sometimes, the skins are pressed during the beam-house operations, thus removing much of the grease before pickling. Hydraulic presses are used and sawdust is sprinkled over the skins to keep them from slipping. The grease is removed by the use of wringers; naphtha is also used to dissolve out the undesirable grease.

When pickled skins, or splits, are received at the tannery, they are first run in a wheel with whiting and salt, borax, or borax and whiting, in order to remove any acid. They are then washed and given a drenching made of bran and salt, after which they are ready for the chosen method of tanning.

37. Tanning of Sheepskins for Rugs, Fur Coats, Etc.—Many sheepskins are tanned without removing the wool, for rugs, mittens, linings for coats, etc. For such purposes, the skins are well soaked in water and fleshed. The wool is washed thoroughly with a solution of soap and soda and rinsed in clean, warm water. The tanning, or tawing, is done by means of mixtures of alum, salt, and saltpeter. The skins may be allowed to soak in the liquor, or the latter is mixed with bran and the paste spread on the flesh side of the skin, which is then folded and allowed to remain in contact with the paste until the tanning is complete. If white skins are not desired, the tanning may be done in a liquor made of hemlock, gambier, or sumac, which should also contain salt and alum. The skins are frequently handled in the tanning solution, and, when tanned, are washed, drained, oiled, dyed, and dried. The alum-tanned skins are frequently worked and stretched while drying, so that when dry they will be soft and pliable.

38. If the skins are to be white, the wool is scoured with a strong soap solution, and the skins are hung in tight rooms and subjected to the fumes of burning sulphur to bleach the wool. Sodium hypochlorite, permanganate of potash, and hydrogen peroxide are also used for bleaching.

In dyeing the wool on either alum- or bark-tanned skins, the wool is first thoroughly washed and rinsed, and the skin stretched on a board. The board is lowered into the dye bath so that the wool is dyed, and the wool is then rinsed, carefully dried, and combed. The wool on bark-tanned skins takes a natural dye from the tanning materials used, and this is frequently the only dyeing it receives.

HOGSKINS

39. Hogskin leather is extensively used for bags, saddles, footballs, etc. It is readily tanned by any of the vegetable-tanning materials. After the beam-house treatment, the skins are tanned in various combinations of oak, hemlock, quebracho, or gambier liquors, in paddle wheels, rockers, or drums. From 6 to 10 days are required to tan the skins thoroughly, and the leather is then cleared, or bleached, by running in a solution of borax or soda, followed by an acid solution, and finally with clear water. It is then given a sumac wheeling, set out by hand, a light coat of oil is given, and then it is dried. After drying, the skins are dampened and shaved, the heavy skins being split. They are then fat-liquored and slowly dried, and allowed to temper for a few days. The leather is then dampened and dyed in a wheel, set out, oiled, and dried. When dry, it is packed in sawdust and staked, or gone over with boarding tool, and after receiving a light seasoning, it is lightly glazed on the machine, when it is ready for shipment.

TAWING

40. For making certain classes of white leather, such as leather for belt lacings, and glove leather, certain agents that are quite different from any previously mentioned, are used. Processes requiring the use of mineral tanning agents were

originally known as *tawing*, but the term has been enlarged and now includes *chrome tanning*.

In tawing, yolks of eggs, flour, alum, and salt are used. The hides treated with these agents become tough and pliable, can be stuffed, and will not decompose.

41. Kid-Glove Leather.—As an illustration of tawing leather, the process for turning lambskins and kidskins into glove leather may be described briefly. The skins are thoroughly soaked in cold water for a couple of days and, when soft, are put into a revolving drum in which are fixed wooden pins that thoroughly shift the skins. Water run through the drum while it revolves thoroughly saturates the skins and removes the dirt. After washing, they are given a long liming in pits, and the excess of lime afterwards removed by thorough washing. They are then unhaired and fleshed. After further washing in the revolving drum, the skins are bated or puered in oropon. After being well washed, they are put into the tanning drum with the tanning liquor. This is generally composed of a mixture of sulphate of aluminum, sodium bicarbonate, salt, flour, egg yolk, and water.

After running the drum from 12 to 15 hours, the skins are taken out and hung up to dry and left in the so-called crust or dried condition for several weeks. This treatment results in a combination of the skin with the aluminum sulphate and the leather becomes thoroughly tanned. On removal of the skins from the crust, they are brought to a sammied condition by dipping in warm water and placing in piles. When in the proper soft condition they are knee-staked by drawing them over a round blunt knife. This knee-staking pulls out the skin to its full dimensions, renders it soft and pliable, and at the same time removes any adhering material left by the tawing treatment.

The well-staked skins are buffed to smooth the flesh side, given another treatment with egg yolk, and allowed to dry. When dry they may be colored or finished in white as desired.

42. Lace Leather.—Another example of tawing is in the manufacture of leather for lacing and whips. The hides are

soaked, depilated in a mixture of lime and sodium sulphide, and, after fleshing and unhairing, are washed and bated. They are then run in a drum with a mixture of alum, salt, sal soda, and bran. After this treatment, they are hung in the loft and dried, and when dry, are wet down and a mixture of neatsfoot oil, linseed oil, and tallow applied. The hides are then dried and, when dry, are slightly dampened and worked by hand or on the machine until they are soft and pliable. After the application of another coat of oil, they are ready for the market.

43. Alum Combination.—Alum-tanned leather, although it is tough, has the disadvantage of being thin and, when wet, becomes hard. To overcome these drawbacks, it is common practice with some grades of leather to retan the skins in some form of vegetable tanning material. This retanning is usually accomplished by running the alum-tanned stock in paddles which contain a solution of gambier. By this procedure it is not necessary to allow the stock to remain in the crust, and the leather may be fat-liquored, colored, and finished in a manner similar to that described for straight vegetable tannage.

44. Pyrophosphate Tannage.—A form of alum tannage which has many points in its favor, consists in adding sodium pyrophosphate to the salt and sulphate of aluminum mixture. The insoluble aluminum pyrophosphate is readily absorbed by the stock and the necessity for crusting is obviated. The skin or sides treated by this process may be dried, sammied, fat-liquored, and finished, or they may be retanned and handled like vegetable tanned leather.

45. Castor and Mocha Leather.—A form of alum-tanned leather which is used very largely in glove manufacture, consists in giving the skins a very long liming, sometimes lasting up to two months. By this long-lime treatment the grain of the skin is loosened and readily removed by means of a blunt knife or stick. The operation of removing the grain is known as *frizing*. The frized skins are then washed, bated, and drenched, and an alum tannage applied. The

tanned leather, after staking and buffing, is finished with a combination of clay and color. This excessive liming, together with the removal of the grain, produces the soft, pliable appearance of this class of leather.

OIL TANNAGE

46. Chamois Leather.—The so-called chamois leather is made from the *fleshers,* or flesh splits, of sheepskins. The splits are thoroughly washed and may be bran-drenched, after which they are pressed to remove the excess of water. They are then thrown into a heavy machine similar to the hide mill used in sole-leather tanneries and worked with cod oil or a good grade of fish oil. Several additions of oil are made while the skins are being worked in the beaters, and the operation of beating consumes much time. When the operation is ended, the skins are removed from the mills, or beaters, and arranged in piles or hung in closed rooms. This causes the skins to heat, completing the oxidation of the oil that has been beaten into the skins. After this treatment, the skins are placed in a hydraulic press and the excess of oil and grease pressed out. The product of this pressing is known as degras and is used in the finishing of many kinds of leather. After this pressing, the skins are washed in a solution of sal soda, which saponifies any remaining oil and grease. The soap thus formed is treated with weak sulphuric acid, which releases the fatty acids. This oil is the sod oil of the currier. After the removal of the oil, the skins are washed, dried, staked, and made smooth and pliable by working, when they are ready for market.

47. Oil-Tanned Sheepskins.—Another example of an oil-tannage production is the old Napa leather, which is really a soap-and-oil-tannage product and not the result of a pure oil tannage, as is chamois leather. The wool is removed from the skins by painting on the flesh side with a mixture of lime and sulphide of sodium, and the skins are thoroughly washed

and then pressed in a hydraulic press to remove the grease. The skins are then run into a revolving drum containing a solution of salt and sal soda, or potash. From this solution, they are removed and pressed, or wrung, and run into a drum with a solution containing soap and neatsfoot oil. When this solution has penetrated the skins, they are removed and pressed. The heavier skins are returned to be retanned, while the lighter skins are colored and dried. When dry, they are moistened and staked and then stretched and tacked on frames and thoroughly dried. When dry, they are buffed, or shaved, and finished to the desired dull or glazed finish.

This leather is soft and possesses considerable strength, being largely used for linings, bookbindings, and as trimming for fancy braces and suspenders.

48. Buckskins.—In the manufacture of buckskin leather, deer skins are the raw material used. The skins are given a long lime treatment, usually extending over forty days. The grain, having become loosened, is removed by frizing and after bating and drenching, they are given an oil tannage similar to that described under Chamois Leather. The finished stock is usually hung out in the air to bleach.

In place of cod-liver oil, it has been found that other oils may be used. The author has been especially successful in substituting the oil from shark liver for cod-liver oil.

49. Lace Leathers.—Lace leather must be especially strong, as it is used for joining machinery belting. A good lace leather may be obtained by milling side leathers out of the bate in a mixture of cod oil and tallow. The milled stock is well set out and allowed to dry very slowly.

50. A process devised by the author and one which is giving very satisfactory results, consists in the use of a combination of alum and oil tannage. The process is carried out by using a short liming process followed by bating with oropon and then pickling with salt and sulphuric acid. The pickled stock is then milled in a 5° Be. salt solution, to which has been

added 7 per cent. of suphate of aluminum and 2 per cent. of borax. The stock, after being milled for 3 hours, is allowed to rest in the exhaust liquor overnight, after which it is set out, and hung up to dry. When bone-dry, the sides are sammied back to a 30 per cent. moisture content and milled with shark-liver oil. The amount of oil required is one-half gallon per side. One-fourth of the oil required is added to the stock in the mill and turned for one hour. A second quarter is then added and milled for another hour, and then the third quarter is added and milled for two hours. The stock is then removed from the drum and piled down overnight. The following day the stock is returned to the drum and the remainder of the oil added. The stock is then run for two hours, and with a lattice door run for another hour. From the drum the stock is well set out, rubbed with shark-liver oil and tallow, and hung up to dry. When thorcughly dry, the sides are sammied lightly and allowed to remain in piles overnight, care being taken that they do not overheat. They are then set out again, rolled, and hung up to dry.

51. Combination Tanned Buckskins.—On the weight of the pickled stock, triturate 5 per cent. of flour with a small amount of water. Dissolve 3 per cent. of sulphate of aluminum and 2 per cent. of salt in 20 per cent. of water. Slowly add to this solution 0.25 per cent. of sodium bicarbonate; mix in 1.5 per cent. of egg yolk and 0.1 per cent. of olive oil. Now add the flour paste. The skins being placed in the drum, the above mixture is introduced, the stock run for two hours, then left in the liquor overnight. The following morning the mill is run for one-half hour, the excess of liquor drawn, and a solution of 10 per cent. of gambier at 19° Bk. with 10 per cent. of salt introduced. The mill is run for 1½ hours. The stock is now fat-liquored with 3 per cent. of acid-fat liquor and hung up to dry. When perfectly dry, the stock is sammied, staked, buffed, and retanned with 5 per cent. of gambier, washed, set out, oiled off with glycerine, and tacked. After stuffing the stock is given a light season of flaxseed liquor and milk, rolled while damp, staked, dried, restaked, and blacked.

CHROME TANNING

52. A typical example of mineral tannage is the chrome process. This tannage is purely a chemical one, consisting of the combination of chrominic oxide with the skin. This combination is evidently a chemical one between the skin and the oxide, as the product is not affected by washing or boiling, as are the products of bark tannages; neither is there any deposition of the oxide after the chemical union has taken place, even in the basic liquors used in one of the processes. Chrome leather is tanned either by the *two-bath process* or the *one-bath method.*

53. Two-Bath Chrome-Tanning Process.—The *Schultz process* of chrome tanning consists in treating the skins to a bath of dichromate of soda in the presence of a mineral acid. Following this, a bath of a solution of soda is given. The theory of this process is based on the formation of chromium oxide, having the formula Cr_2O_3, which is deposited on and combines with the skins. A solution of dichromate of soda and hydrochloric acid is made up in the proportion of about 5 pounds of dichromate and 2.5 pounds of hydrochloric acid, specific gravity 1.16, to every 100 pounds of wet prepared skins.

The reaction expected between the acid and the dichromate is

$$Na_2Cr_2O_7+2HCl=2NaCl+H_2O+2CrO_3$$

However, in the process, only two-thirds of the acid necessary for the complete reaction, is used, and it is not safe to say, considering the peculiar properties of chromium, that this equation exactly represents the reaction which takes place.

After the skins have been struck through in this bath, they are put into a solution of thiosulphate of soda and hydrochloric acid, which effects the reduction of the CrO_3 to Cr_2O_3. To neutralize the acid remaining in the skins, they are afterwards wheeled with water containing suspended calcium carbonate, or a solution of borax or sodium bicarbonate.

54. The use of practically all the agents that will reduce CrO_3, as hydrogen sulphide, the sulphides, bisulphites, etc., has been patented. Sulphurous acid seems to be the best, or, at least, it is one of the most generally used. Norris has patented the use of zinc in the hypo bath, which, it is claimed, accomplishes a more rapid and economical reduction.

By using sodium dichromate and sulphuric acid, it is possible to effect the reduction with sodium bisulphite and thus eliminate the production of free sulphur as is the case where sodium thiosulphate and acid are employed in the reducing bath.

Amend has a two-bath process in which chromic acid, H_2CrO_4, replaces the dichromate and an acid of the Schultz patent. This requires careful manipulation. He suggests the use of aniline as a reducing agent.

A chalk bath after the tanning bath neutralizes the hydrochloric and sulphurous acids remaining in the skins. Solutions of sal soda, sodium bicarbonate, and borax are also used for the same purpose. Norris has patented the use of potassium permanganate for this purpose. This salt not only oxidizes the sulphurous acid to sulphuric acid and neutralizes it at the same time, but it also precipitates the oxide of manganese on the skin, and this acts as a mordant in subsequent dyeing.

55. One-Bath Chrome-Tanning Process.—The one-bath chrome process of chrome-tanning, brought to perfection by Martin Dennis, and now used by many manufacturers, offers less difficulty than the two-bath system and has largely replaced it for all grades and classes of stocks excepting goatskins.

In this process only one bath is used; this is composed of a solution of a basic chrome salt that readily yields its excess of chromic oxide to the hide tissues. The tanning liquor, as originally prepared, was made by dissolving oxide of chromium in hydrochloric acid, thus forming the normal chloride. To this was added an alkaline base, as sal soda, this stronger base taking from the chromium chloride part of its acid, leaving

the oxy, or basic salt. This basic salt is a very unstable compound and readily yields its excess of chromium to anything having an affinity for it, which, in this case, is the hide substance. The advantages of this system over the two-bath system are as follows:

1. One handling of the skins is saved, because one bath only is needed for the tanning.

2. The skins are not exposed to the destructive action of chromic acid, and are therefore stronger, with more lasting suppleness, and have a better grain.

3. There are no offensive fumes evolved in this process; the reduction of the oxide in the two-bath process is accompanied by a strong odor of sulphur dioxide.

4. The skins are not harmed by too long contact with the tanning liquor.

5. Less skill is required to operate it and the bath itself is cheaper.

56. The practical operations of tanning by means of the one-bath system are as follows:

The skins or hides are soaked, limed, unhaired, fleshed, and bated as usual. From the bate they are taken to a drum and pickled with a solution of salt and sulphuric acid in the proportion of 12 per cent. salt with $1\frac{1}{2}$ per cent. of sulphuric acid at a density of 12° Be. This keeps the skins open and plump and also has the effect of keeping them in good condition during and after tanning. From the pickle they are put in the tanning bath, which contains a solution of the concentrated basic chrome liquor, 3 per cent. of Cr_2O_3 on the weight of the stock, and also 10 per cent. of common salt. This common salt prevents the grain of the leather from drawing under the astringent action of the chrome bath.

When the skins have assumed a uniform greenish-blue color and a cutting reveals the completion of the process, they are neutralized with 1 per cent. of sodium bicarbonate and horsed up overnight. The next day they are rinsed in clean water and worked on the flesh side with a slicker on a perfectly

clean table or they are set out on the machine. They are next shaved and sorted for colors and blacks.

57. Since Martin Dennis made practical use of one-bath chrome liquor, many other concerns have entered the field. As a result of investigation, many methods for preparing one-bath chrome liquors have been developed. The simplest method of preparing this liquor, and the one used by many tanners, consists in reducing sodium dichromate in the presence of an acid. A formula which gives very satisfactory results is as follows:

Dissolve 20 pounds of sodium dichromate in 25 gallons of water. To this add 10 pounds of sulphuric acid and 20 pounds of salt. In a separate container dissolve 22 pounds of sodium bisulphite in 10 gallons of water, and add this solution very slowly and with constant stirring to the solution of chrome. The resulting liquor should be blue-green in color; if not, a little more sodium bisulphite should be added. When completely reduced, add enough water to make 40 gallons and use this as a stock solution. To tan with this liquor, use 8 gallons for each 100 pounds of the pickled stock.

58. Characteristics of Chrome Leather.—Chrome leather has special and peculiar qualities that distinguish it from other kinds of leather and which make it a superior article. It is not actually waterproof, but rather a moisture resister. It is a difficult matter to wet it thoroughly when once perfectly dry.

The ordinary bark tannages are compounds of two organic materials and when they are subjected to alternate wetting and drying, they will eventually deteriorate and become rotten. Chrome leather, being a combination of an inorganic material with the hide substance, is not affected by wetting and drying. It is lighter than bark leather and also possesses more elasticity and is of greater strength.

59. Chrome Combination.—For certain uses straight chrome leather does not answer all of the requirements. Tanners have, therefore, found it desirable to after-treat or retan

the chrome stock. This is done by running the skins in a solution of some vegetable tanning material. The so-called washable cape leather used extensively in glove manufacture is produced by first tanning the skins in chrome and subsequently retanning in gambier extract. The skins are then well fat-liquored, dried, sammied, staked, buffed and colored.

60. Fat-Liquoring.—The finishing, or currying, of chrome leather is carried out with some modifications of the methods used for finishing bark leather. Chrome leather must be stuffed soon after removal from the tanning bath and must not be allowed to become dry. The most efficient way of stuffing chrome-leather is by *fat liquoring*. There are different ways of making and using these fat liquors, depending on the quality of the leather to be produced.

The fat liquor most commonly used consists of some form of sulphonated oil which produces an emulsion with water and which is readily taken up by the stock. Soap mixed with neatsfoot oil is very largely used in the fat-liquoring of goatskins for glazed kid. Either sulphonated oil or soap may be employed to carry in other materials such as egg yolk, degras, cod-liver oil, and the like. The amount and nature of the oil used regulates the character of the finished product; the more oil employed, the softer will be the resulting leather.

61. There are on the market many varieties of chrome leather that are sold under different trade-names. When these varieties of leather represent the product of straight chrome tannages, the actual tannage of each particular brand is carried out in the same way, the differences that characterize them being due to the amount and character of stuffing, character of the finish, and the style of grain given the finished leather.

62. Box Calf.—The variety of leather known as box calf is generally made in the following manner: The skins are soaked, limed in a mixture of lime and red arsenic, or of lime and sodium sulphide, fleshed, unhaired, and bated. They are then pickled in a solution of sulphuric acid and salt and

tanned by either the one-bath or the two-bath chrome process. The skins are then pressed in a hydraulic press, or worked out by hand or machine, and shaved to give the flesh side a smooth surface. They are then stuffed, or fat-liquored, and colored. After hand or machine setting out, to remove the excess water, they are dried simply by hanging them over poles in the loft. When the leather is dry, it is packed in damp sawdust, and when properly sammied, it is staked by machinery. The well-staked skins are then tacked out on frames and allowed to dry under tension. When thoroughly dry the skins are *stripped* from the boards and given a coat of season. This season may be made up in several ways but usually contains some gelatinous or albuminous material to which coloring matter has been added. The commonest color is black and is produced by adding a solution of logwood and iron to the compound. The skins after seasoning are hung up to dry. When the season has become set and the skins are thoroughly dry, they are glazed on the machine and a second coat of season applied. The skins are again glazed, which operation may be repeated several times before boarding. The *box* grain of the leather is given by a workman, who has a cork-covered boarding tool strapped to his forearm. The boarding tool is applied to a fold of the leather, and the characteristic grain imparted to the leather by the motion and pressure exerted by the workman.

63. Bright Finish Calf.—In producing a bright finish on chrome calf, the same operations are carried out as for box calf, except that a shorter liming is applied and the final glaze finish contains either blood or egg albumen. The operation of boarding is, of course, omitted.

64. Matt Calf.—When a dull finish is required, the same operation is carried out as for bright finish except that the season employed does not contain any albuminous material. The dull effect is produced on a smooth plate machine or by the application of a hot flatiron. After ironing, the stock is oiled off with a light mineral oil which gives the final pleasing appearance to the leather.

65. Glazed Kid.—Goat skins, usually imported in a dried state, are used in making both glazed, white and dull kid, although some sheep leather and even some light grain splits are sold to be used in *glazed-kid shoes*. The dried goat skins are well soaked and then painted on the flesh side with a mixture of sodium sulphide and lime. This attacks the roots of the hair, loosening it, and causing it to slip easily. After painting, the skins are folded along the spine, flesh side in, and piled in low piles to lie overnight. In the morning the hair is removed and the skins limed. In the lime liquor a mixture of lime and red arsenic is used. The skins after beaming are washed in paddle wheels to remove some of the lime and sodium sulphide used for unhairing. After fleshing, the skins are bated, or puered, with dog-manure or oropon to the proper condition for tanning. Either the one- or the two-bath chrome process is used for tanning, the latter being the more popular. After being run in the first bath in a drum, the skins are removed and set out on a machine, or pressed in a hydraulic press, to remove the excess of liquor. They are then dipped by hand in a solution of hydrochloric acid and hyposulphite of soda and placed in covered piles. This hand-dipping is for the purpose of reducing some of the chromium solution on the surface of the skins. The next day the skins are taken from the piles and run in a drum with the second bath, which reduces and fixes the chromium oxide on the fibers. Some tanners prefer to neutralize in a paddle rather than in the drum.

66. When the reduction is complete, the skins are run with sodium or bicarbonate solution until the free acid has been neutralized, and finally they are washed with clean water. The skins are then set out by hand or by machine to remove the excess of water, fat-liquored, and given the desired color, after which they are worked by hand or machine to remove moisture and to give them a soft silky grain and also to stretch them. The skins then receive a light coat of glycerine, or of glycerine and oil, on the flesh side and are dried on poles in a warm drying-loft. When thoroughly dry, they

are taken to an airy loft, thrown in piles, and left to temper for 7 or 8 days, during which time they absorb atmospheric moisture, and soften. After tempering, the skins are packed in damp sawdust, which brings them to a proper condition for staking. The staking is done either by hand or by machine, the smaller and lighter skins being generally hand-and-knee-staked, while the machine is used on the larger and heavier skins. After being thoroughly broken and softened by the staking, a coat of heavy seasoning is applied, and after this is dry the skins are lightly glazed on a glazing machine. Seasonings vary in composition with the finisher, but they are generally compounds of such materials as blood albumen, egg albumen, algin, etc., and are colored to match the color of the leather that is being finished. After the first seasoning and glazing, a second coat of lighter seasoning is applied, and the leather receives a heavier glazing on the machine. A final light coat of seasoning is applied, and the skins are then glazed with a heavy pressure, after which they are laid away to be inspected, sorted, measured, and packed for shipment.

67. For dull-finished leather, a heavier stuffing, or fat-liquoring, is given the most perfect of the skins and, instead of being glazed by the machine, they receive a light coat of paraffin oil and are ironed by hand with a hot flatiron. They may then receive another coat of oil and receive a final ironing.

68. Chrome side leather is made by soaking, liming, unhairing, fleshing, and bating the whole cowhide, and then pickling it in salt and sulphuric acid, and splitting. The grain split is then chrome-tanned and the subsequent finishing processes are the same as for either glazed or dull kid. Heavier grain splits may be tanned and finished in a manner similar to that employed with chrome calf, and frequently the entire cowhide is chrome-tanned before splitting.

69. Chrome Patent Leather.—Whole skins, such as calf, goat, and kid, or split cowhides and steer hides are used in making *enameled*, or *patent, leather* for shoes. The actual tanning processes for leather to be coated are similar to the

methods of tanning different skins or hides into other light leathers. The fat-liquoring and seasoning vary somewhat, but up to the point of enameling, the process is not materially different.

70. A patent shoe leather made from chrome-tanned cowhide splits is made by the following process: The hides are soaked, split into sides, fleshed, depilated with lime and sodium sulphide, washed, and bated. They are then pickled in a solution of sulphuric acid and salt, and are either pressed or put through a wringer and then sent to the splitting machine. The grain split is used for making the patent leather, and after being shaved on the machine to give it uniform thickness and to make the flesh side smooth, it is tanned by a one-bath chrome process. It is then fat-liquored and colored, the flesh receiving a purple color before the main dyeing takes place. After setting out by hand or on the machine, the grain side receives a light oiling, and the split is then sent to the loft and dried. When dry, it is packed in wet sawdust, then staked by the machine and carefully tacked. The leather on being stripped is usually degreased and is then ready to receive the enameling compounds. These are made in various ways, the pastes used on the first coats being generally made by boiling down linseed oil with lampblack and adding naphtha to thin them. Other oils and mixtures are used for this purpose, their ingredients differing with each foreman, who endeavors to keep his competitors from securing his formulas. The leather is stretched and tied to frames, after which the first coat of daub is rubbed on and worked over the surface evenly, all surplus being removed by means of a slicker. When the first coat has dried, a second coat of the same material is applied in the same manner, and the frame, with the leather, is placed horizontally in a large oven to dry. If other coats are to be applied before the top varnish, they are put on after this drying and the frame returned to the oven. When the leather is ready for the top varnish, it is gone over with pumice to make the surface perfectly smooth and to remove pimples. The dust from this operation is brushed off the leather, or

blown off by a jet of compressed air. The top varnish is applied in a warm, dust-proof room, into which the ovens open. It is thinner than the previous coating solutions and varies in composition. Linseed oil, organic gums, pyroxylin, or guncotton, camphor, amyl acetate, wood alcohol, and castor oil are among the ingredients of the various daubs and varnishes used for coating leather, and probably no two factories use the same formula. The top varnish is applied to the leather with a broad, long-bristled brush similar to a white-wash brush. In applying this top coat, great care is taken to spread it evenly and to leave no bubbles or dust or hair marks.

After receiving the top varnish, the frame is placed in the oven and the skin dried, and after the oven drying it is taken into the air to receive a final sun-and-air drying, which removes any tendency to stickiness. When thoroughly dried, the finished leather is cut from the frame, trimmed, and measured, when it is ready for shipment.

71. Chrome sole and belting leathers are being made in constantly increasing quantity, although as yet this class of tannage has not become common. The sole and belting leather produced by the chrome-tanning process has not the weight of the bark-tanned leather it aims to supersede, and its cost is accordingly higher. The cowhides or steer hides from which these kinds of leather are made, go through the regular beam-house processes, being bated so that all the lime is removed from the hides. Then they are pickled in a solution of sulphuric acid and salt, and when drained after removal from this solution they are ready for the tanning. The one-bath chrome process has been found most suitable for this class of leather. The pickled hides are usually tanned on the paddles, as the constant tumbling of such heavy stock in a drum is apt to produce a loose grain. The liquor is first made up by preparing a 10° Be. salt solution and then adding an excess of the one-bath chrome liquor. The time of the treatment varies from 12 to 48 hours, depending upon the nature of the tan liquor. A few tanners carry on the operation in rocker pits, but such practice is not very common.

After being tanned so as to stand the boil, the hides are removed from the paddle and horsed up overnight. They are then shaved, neutralized, washed, and fat-liquored. For sole leather the fat-liquoring is only slight and some tanners do not give the hides any oil. Where the stock is fat-liquored, it is tacked while still wet and allowed to dry under tension. This drying under tension results in a stiff leather which is desirable for this kind of stock. If the leather is to be made waterproof, it is dipped into hot wax and immediately transferred to the hot room to drain. Some shoe manufacturers prefer to purchase the chrome sole and do their own waterproofing.

When heavy chrome leather is to be used for belting purposes, it is fat-liquored somewhat higher than sole leather but is afterwards dipped to make it stronger and more waterproof. In place of tacking, leather to be used for belting is usually cut in strips and dried under tension in stretching frames.

72. Chrome Combination.—Straight chrome sole leather is more difficult to work then vegetable-tanned stock and does not channel or buff very satisfactorily. This objection may be overcome by retanning the hide with a vegetable tanning agent. A ten-day treatment with 40° Be. extract will fill the stock, add weight, and improve its appearance. Stock which has been retanned in this way may also be loaded in the extract wheel and made to carry considerable weight. Chrome retanned leather is usually waterproofed in the same manner as straight chrome. Chrome retanned sole leather may be worked like vegetable-tanned stock and can be channeled and burnished with ease.

DONGOLA LEATHER

73. An example of a combination vegetable and mineral tannage is found in the so-called *dongola leather.* Originally, the dongola tannage was a combination of alum and gambier, but dongola leather is now made with vegetable combinations other than gambier. Hemlock and oak liquors are sometimes

used in combination with gambier, and quebracho extract is also a popular material for use with gambier. This class of tannage is applied to calfskins, sheepskins, goatskins, kidskins, and side leathers.

74. Preparation of Dongola Leather.—After coming from the beam house, the skins are bated and washed and then pickled in a solution of sulphuric acid and salt. After pickling, the skins go into the tan liquor, which is made up of gambier, gambier and quebracho, gambier and hemlock, etc., to which is added a solution of alum and salt. The tanning takes place in rockers or in paddle-wheel vats. In some tanneries, the stock is given the mineral and then the vegetable tanning, the skins being first tawed in the alum and salt liquor and then tanned in the vegetable tan liquor.

After tanning, the leather is washed in a wheel, pressed or wrung, and then shaved; if splitting is necessary, it is done at this stage. Sometimes, the heavy hides are split out of the pickle, the flesh splits being tanned by a dongola process, while the grains are finished by a chrome process.

After shaving or splitting, the leather generally receives a wheel treatment with a pure gambier or sumac liquor. Splits are retanned in gambier or quebracho liquor in a wheel, or they may be returned to the original tanning vats.

From the sumac wheel, the leather is piled on horses and allowed to drain overnight; or, it may be set out immediately and then stuffed. The stuffing is done by a fat liquor generally made of soap, cod oil, and degras. Frequently, the leather is given two stuffings, the first being a straight-oil combination, such as neatsfoot and cod oils. Then, after drying and redampening, the leather is again stuffed with a fat liquor. After stuffing, the leather is dried. When dry, it is dampened in a wheel with warm water and is then colored and finished according to the character and appearance desired in the finished product.

LEATHER DYEING

75. Dyeing and Finishing of Leather.—Dyes are applied to leather by brushing by hand or on the machine, by means of the paddle, or mill, or on the tray. In the brushing method a solution is spread evenly over the grain on the flesh side by means of a stiff brush and then hung up to dry. In tray dyeing the skins are either folded down the back or two skins are placed flesh to flesh and then drawn several times through the color solution. When a large number of skins or sides are to be dyed the same color, the paddle or mill is employed. In paddle coloring, the necessary quantity of dyestuff is dissolved in the water and while the paddle is turning the stock is carefully introduced. By far the largest amount of leather is colored in the mill, in which case the skins are placed in the drum and enough water introduced to cover the stock. The mill is then set in motion and the color solution slowly added through the trunnion.

In coloring leather both natural dyewood extract and coal-tar colors are applied. Of the natural dyes, logwood, fustic, and osage orange are most commonly used. Of the coal-tar colors, basic acid, direct and alizarine dyes are employed.

As the methods used for coloring chrome-tanned leather may be applied equally well to vegetable-tanned stock, we will illustrate the various procedures on this kind of leather.

76. Black.—The shaved stock, after being weighed, is placed in the mill and enough water at 125° F. added to float the skins. One per cent. hematin on the weight of the stock is dissolved in water at 125° F. and, being made alkaline with ammonia, is introduced through the trunnion while the drum is in motion and turned for fifteen minutes. One and a half per cent. of direct leather black is dissolved in water at 145° F. and added through the trunnion to the contents of the drum and run for 15 minutes longer. Without removing the excess of color, a sulphonated oil fat-liquor is introduced into the mill turned for another half hour. The stock is then washed, oiled off with Setine No. 2 and hung up to dry.

77. Dark Tan.—The shaved stock is placed in the mill and sufficient water added at 125° to float the stock. While the mill is in motion a solution 3 per cent. of fustic is introduced through the trunnion and the milling continued for one-half hour. A solution of one-fourth of one per cent. of potassium titanium oxalate is now added and run for 15 minutes. The stock is then washed for 5 minutes with warm running water, enough being allowed to remain to float the stock, and the following dye solution introduced. For each 100 pounds of skins make up

Flavo phosphine G. G. Conc., 22 oz.; vesuvine R., 3 oz.; methylene blue B., ¼ oz.; water at 140° F., 10 gals.

While the mill is in motion one-third of the color is introduced through the trunnion. At the expiration of 5 minutes a second third is added, and after another 5 minutes the final portion is introduced. The mill is then run for one-half hour, the stock washed in running water and fat-liquored with a good grade of sulphonated oil. The skins should then be set out carefully and hung up to dry.

78. Dyeing with Acid or Direct Colors.—The shaved skins are placed in the drum and sufficient water added at 125° F. to float the stock. The color solution is prepared by dissolving the necessary quantity of dyestuff in water to which is added about 1 per cent. of borax. The color solution is introduced in 3 portions and the stock milled for one-half hour. By this time the color has penetrated the leather and is set by adding 3 per cent. of formic acid diluted with water and run for 15 minutes. The excess of color is drawn off and the stock fat-liquored with sulphonated oil. The skins are then set out and hung up to dry.

79. Sammie.—The skins as they come back from the dry-room are stiff and so must be softened back. This is done either by dipping in warm water and placing in piles to sammie or they are packed down in damp sawdust for several hours.

80. Staking.—In order to stretch the skins they are worked in a staking machine.

81. Tacking.—After staking the skins are sent to the tacking loft and while still damp are carefully tacked on frames and allowed again to dry.

82. Finishing.—On stripping from the frames the skins are given a coat of season and while slightly damp, are rolled on the jack. They may then be finished in matt or bright as desired by using the proper solution and either ironing or glazing.

MEASUREMENT OF LEATHER

83. Sole leather is always sold by weight, but light leathers are sold by area, the approximate thickness also being taken into consideration. The measurement of leather is now

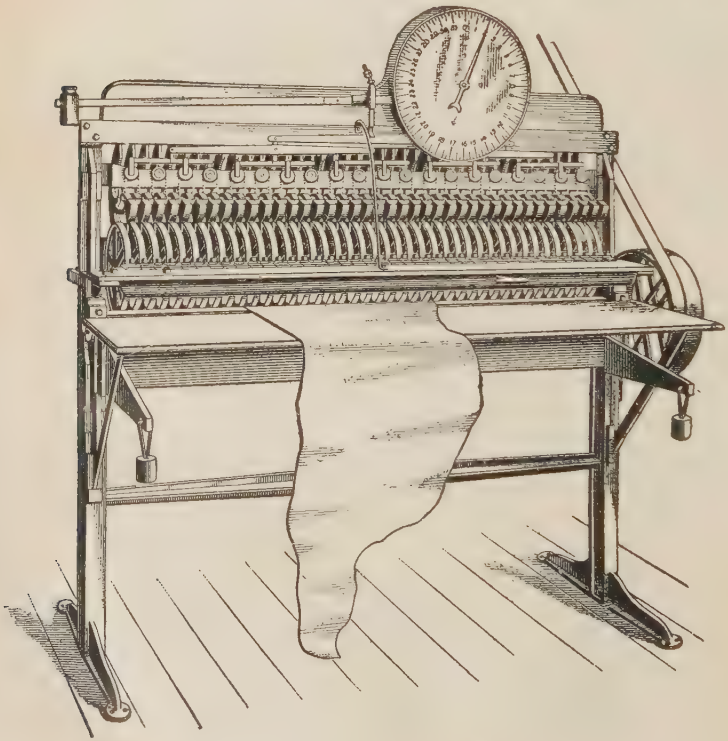


Fig. 13

usually done by means of machines, of which there are several on the market. Some of these vary essentially in principle, but the descriptions of the Sawyer and Union measuring machines given here will be sufficient to show their application.

84. Sawyer Measuring Machine.—The Sawyer leather-measuring machine, shown in Fig. 13, is run by power. The leather is fed between two rollers that smooth it out and bring it into contact with small measuring wheels. The movement of these wheels influences properly arranged levers, which, in turn, affect the index of the registering mechanism.

85. Union Measuring Machine.—The Union leather-measuring machine, shown in Fig. 14, consists of a table with a top made of parallel sticks of wood. A hinged cover closes

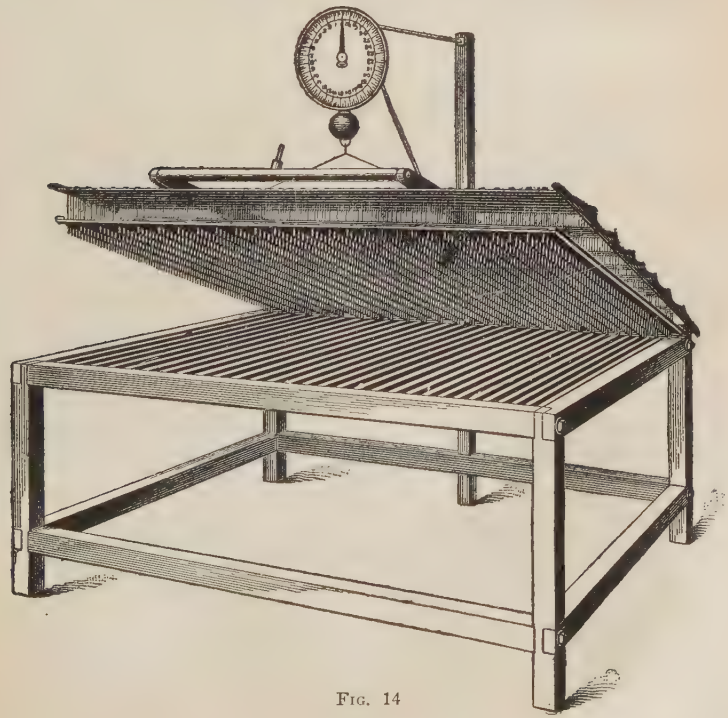


Fig. 14

over this, and throughout the entire surface of this cover are suspended small wire pins that are free to slide up through holes in the cover. The pins are arranged in rows, so that when the cover is down, with nothing between, the pins hang between the strips of wood forming the lower table.

When leather is to be measured, it is placed on these strips and the top brought down over it. The surface of the leather obstructs the small pins and throws them up, the ends of the remaining pins dropping between the strips. These pins are of such sizes and weights that each exercises the same force on a spring balance above, so that this device is affected by the number of pins obstructed by the leather. The weight of forty-eight of the pins corresponds to a square foot of area, and the dial of the balance indicates, in fractions of a square foot, the weight released by the leather, and consequently the area of the leather.

MANUFACTURE OF SOAP
(PART 1)

INTRODUCTION

1. Definition of Soap.—Soap, strictly speaking, is the compound of an alkali, either sodium or potassium, with the higher fatty acids, especially with oleic, palmitic, and stearic acids. The insoluble compound of a fatty acid with a heavy metal is, however, technically called a soap. The chemist is familiar with the lead soap or lead plaster of the pharmacy, with alumina soap used as a thickener of lubricating oils, and with iron and chromium soaps used in dyeing and in the color printing of textiles.

As commonly known, soap is, according to its quality and the use for which it is intended, a mechanical mixture of the compound just described with varying proportions of water, with soluble alkali compounds of the rosin acids, with sal soda, $Na_3CO_2 10H_2O$, with sodium silicate or soluble glass, or with other inert, detersive, or odoriferous agents, incorporated for the purpose of cheapening the product, improving its appearance, increasing the detersive action, or overcoming the natural odor with an agreeable perfume. Therefore, commercial soap is a mixture of pure soap with a diluent, as water; with body-imparting substances, as talc, starch, or a petroleum residue; or with detersive agents in aqueous solution, as sodium carbonate, borax, or sodium silicate. These additions may all be present in a single soap, but the nature and amount of the additions present depend on the character of the soap itself and on the purpose for which it is intended.

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

2. Classes of Soap.—There are three general classes of soap, namely, industrial, household, and toilet. In the first class are included so-called textile soaps used in the process of manufacture of cotton and woolen goods. In the second class are included the soaps that are consumed in various qualities and conditions by the laundry trade; and in the third class shaving and medicinal soaps may conveniently be included. The manufacturing of soap powder, scouring powder, and glycerine is generally associated with the soap industry.

The discussion of the subject that follows will deal with the process of manufacture rather than with the use for which the product is intended.

GENERAL OUTLINE OF THE MANUFACTURE OF A SETTLED SOAP

3. The following outline gives a general idea of the various operations performed in the manufacture of a settled laundry or domestic soap. The relation of the different operations to one another is here made clear, and the following detailed descriptions of the different operations and processes rendered more intelligible.

Source of Fatty Acids.—In the definition of a soap just given, it was stated that a soap is a salt formed by the union of an organic acid of the higher fatty series with a metal, usually an alkali metal. The acid portion of soaps is derived from various animal and vegetable fats and oils, which are compounds of the organic acids just mentioned with glycerine.

Soap Stocks.—Any fat or oil used in the manufacture of soap is called a *soap stock*, and may be of either animal or vegetable origin. The various kinds and grades of soap stock used will be fully discussed later.

Saponification.—The operation by which oils and fats are combined with the alkali metals sodium or potassium to form soaps is called *saponification*. Technically, this term has a wider meaning, and applies to any operation that brings about a separation of an organic acid from an organic base.

When an animal or a vegetable fat is boiled with a caustic alkali, a double decomposition takes place. The products are the alkali salts of the organic acids of the fats and glycerine.

Graining and Settling.—After the saponification is complete, the soap is *grained*, or brought into a somewhat granular condition, by the addition of certain salts or alkalies in whose solutions the soap is practically insoluble. When in this granular state, the soap separates from the impure liquor, or lye, which may be drained off.

Crutching.—The soap, after the preceding treatment, is introducted into a machine called a *crutcher*, where it is crutched, or stirred, until it is thoroughly mixed. Here, fillers, perfumes, etc. are introduced and incorporated into the soap.

Framing.—From the crutcher the soap is run by gravity to a rectangular box, called a *frame*, of proper dimensions, in which it is allowed to stand until it is of a consistency suitable for cutting into slabs and bars.

Slabbing.—The mass of solidified soap from the frame is first cut horizontally into slabs. This operation is called *slabbing* and is performed on a machine called a *slabber*. These slabs in turn are cut, on somewhat similar machines, into blocks of suitable dimensions for making finished cakes.

Drying, Pressing, Etc.—The rough blocks are now dried superficially until a thin skin is formed over them. They are then pressed into finished cakes in dies and wrapped and packed for shipment.

RAW MATERIALS OF SOAP MANUFACTURE

ANIMAL SOAP STOCK

4. Animal soap stock occurs on the market in a variety of grades, depending on its origin and method of preparation. This stock constitutes the chief fatty material used by the soap maker. According to the part of the animal from which it is obtained and the method of rendering, it may be classified as tallow, bone stock, and grease. These classes of animal soap stock may again occur in various grades. In determining the quality, buyers, as a rule, depend on the simple tests of color, odor, and grain, supplemented by the titer, or hardness test, which will be described later. In addition, the percentage of moisture, unsaponifiable matter and the percentage of free fatty acids are determined. The last determination is of especial importance when the stock is considered with relation to its yield of glycerine.

5. Tallow.—The tallow used in soap making varies in its composition according to the part of the animal from which it is obtained and the nature of the food used in fattening the animal. Corn-fed cattle produce the firmest fat. The fat of mast-fed cattle is not so firm as that obtained from animals fattened on oil cake. Tallow consists of stearin, olein, and palmitin.

6. The percentage of free fatty acids is not only a reliable index of the quality of the stock used by the renderer but is a telltale on the care that he has employed. The following conditions conducive to the formation of a high percentage of free fatty acids in the various grades of tallow may be enumerated:

1. Allowing the raw material to stand before rendering, especially in warm weather. After the death of the animal,

decomposition immediately sets in, and the first step in the decomposition of tallow is the separation of the fatty anhydrides from the glycerol, which is immediately followed by the decomposition of the glycerine and its loss as such.

2. An excessively high temperature in rendering tends to increase the percentage of free fatty acids. The presence of water in the tissues and the influence of the high temperature in the rendering tank tend to the hydrolysis of the glyceride.

3. Rendering in closed vessels increases the percentage of free fatty acids. It will be clear that conditions prevail here that are purposely introduced and maintained in the process for the saponification of glycerides with steam under pressure in the manufacture of fatty acids and glycerine.

4. The season of the year has a great influence on the percentage of free fatty acid in even high-grade tallows, as the table given herewith will show. These figures are taken from a whole year's consumption of the best average tallows used in a factory making a high-grade laundry soap. In determining the value of a tallow the season of the year must always be taken into consideration in respect to the free fatty acid.

Month	Lots	Free Fatty Acids Per Cent.
January	58	4.31
February	55	4.09
March	61	4.27
April	63	5.28
May	47	5.36
June	63	6.39
July	53	8.03
August	81	8.19
September	68	7.28
October	63	7.01
November	54	5.12
December	75	4.58

The significance of the free-fatty-acid determination will be fully shown when the various fats and oils are discussed

with reference to their content and yield of glycerine and the changes incident to saponification.

7. Bone Stock.—Bone stock is intermediate in quality between tallow and grease and is obtained from fresh bones by rendering in a closed vessel under pressure.

8. Grease.—The commercial term *grease* is applied to all fatty material of animal origin that cannot be classified among such distinctive products as tallow, lard, etc. It is obtained from hides, kitchen refuse, recovered garbage, offal, dead animals, etc.

White grease is made directly from hog fat and trimmings and has a large use in the manufacture of white toilet soap. Owing to its high percentage of olein it produces a soap much softer in body but with better lathering qualities. *Dark*, or *house* greases, as they are called, produce a much darker soap and are used mainly for soap powder soaps. With dark greases a boiling process and not a cold process should be employed, however, because it is necessary to remove the dark coloring matter and other impurities with the waste lyes, and also to eliminate all disagreeable odors.

MANUFACTURE OF ANIMAL SOAP STOCK

9. In the manufacture of animal soap stock the various grades of tallow are extracted from the fat-enclosing tissue that surrounds the intestines, muscles, and other organs of the animal. The feet yield neatsfoot oil. The process of rendering consists essentially in the separation of the fatty matter from the enclosing animal tissue. Tallow was originally obtained by boiling the finely divided parts of the animal containing the fat in water and skimming from the surface of the water the fat thus disengaged from the membrane. Fleshy portions of the animal previously finely chopped and rendered in the manner just mentioned yield the kettle-rendered tallow used for edible purposes. Tallow, not of packing-house origin, is usually distinguished as country or city rendered.

10. Steam Rendering.—Steam-rendered tallow is obtained by subjecting the rough fat to a steam pressure of 30 to 60 pounds per square inch in a closed vessel, such as is shown in Fig. 1. The top of the tank is on the floor level and is provided with a safety valve, a manhole *a* for introducing the rough fat, which is commonly conveyed in barrows, and a discharge pipe for the exit of fumes. Near the middle of the tank are two draw-off cocks (not shown in the figure) for the removal of the liquid tallow. Water is admitted through a valve near the bottom. At the bottom of the tank is either a large gate valve *b* or a tightly fitting door for the discharge of the "soup." The *soup*, or *soup liquor*, as it is called in the packing house, consists of soft bones, solid residuum, and water highly impregnated with albuminous matter. The liquid portion is run off and evaporated to a sirupy consistency under a partial vacuum, and is afterwards mixed with the solid matter freed from an excess of liquor by compression in a fertilizer press. This material constitutes the tankage fertilizer of the packing house.

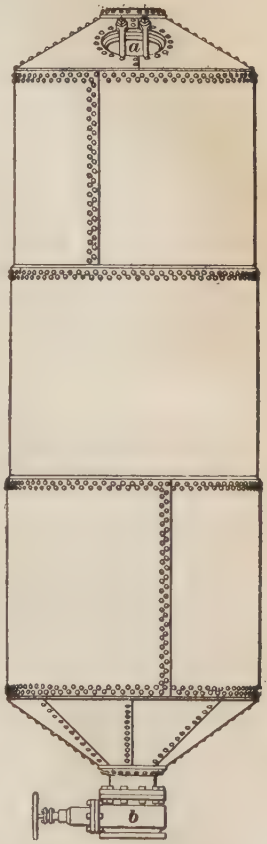


Fig. 1

After charging, these tanks, which are usually arranged in a series, are tightly closed. Water is run in, if desired, and steam is turned on. The period of working varies from 4 to 10 hours, according to the size of the tanks, the quantity of material introduced, and the steam pressure. At the expiration of the rendering period, the fat is discharged by means of the draw-off cocks. When the last portions of fat are below the level of the draw-off cocks, water is admitted into the tank

from below, and the fat floating on the surface of the water is thus completely discharged. The remaining contents of the tank is then dropped through the discharge gate at the bottom.

11. Chemical Rendering.—While most of the animal stock used in the manufacture of soap is prepared by the steam-rendering process, chemical rendering is carried on to a considerable extent. For this purpose, dilute liquors of either sulphuric acid or caustic soda are used, and the odorous substances present in the stock become partly destroyed or combined with the chemical agent used. If the acid process is employed, wooden or lead-lined tanks must be used for the operation.

VEGETABLE SOAP STOCK

12. Any vegetable oil may be employed for the manufacture of soap, its applicability for this purpose being determined by its character, cost, and the intended use of the soap made from it. Except in making soft soap or soap for special purposes vegetable oil is seldom used alone. However, oil of some character finds its way into most every soap charge. Linseed oil and the various nut oils—peanut oil, for example—cannot compete with cottonseed oil because of their greater initial cost, although in cases of very large flax crops linseed oil has been cheaper than either cottonseed or corn oil. Castor oil is used but little, its very limited consumption being confined to the manufacture of transparent soaps. Linseed oil is used extensively in Europe in the manufacture of soft soap. In the United States soft soap finds only limited sale as a detergent. The soft soaps used in the cotton and woolen industries are made from a non-drying glyceride base. In Table I is given the average percentage yield of oils of vegetable origin. The percentage yield of oil from seeds, fruits, etc. is dependent on a variety of conditions, chief among which are the character of the soil, the weather, and the degree of ripeness, and these are subject to extreme variations. These conditions influence, as well, the specific gravity of one and the same oil. Moreover, according

to the age, mode of preparation, etc., of the oil, the variations in specific gravity may be as great as the difference between the density of one oil and that of another serving as an adulterant.

13. Cottonseed Oil.—The chief product of cottonseed, which constitutes about two-thirds of the weight of the unginned cotton grown in the Southern States, is cottonseed oil. In recent years, this oil has attained great importance as a soap stock, although its use in this connection is small compared with its consumption for edible purposes. Crude cottonseed oil is a thick, reddish-brown to black oil of extremely

TABLE I

YIELD OF OIL FROM VARIOUS SEEDS, NUTS, ETC.

Seed	Percentage Yield of Oil	Seed	Percentage Yield of Oil
Castor (Indian) . .	51–53	Maize, or corn . . .	6–10
Castor (American)	46–49	Olive (pericarp) . .	40–60
Coconut	40–45	Palm (pericarp) . .	65–72
Colza, or rape	33–43	Palm kernel	45–50
Cottonseed	24–26	Peanut	43–45
Linseed	38–40	Sesame.	50–57

varying quality, depending on the season and the care exercised in the collection and storage of the seed. The crude oil contains from 10 to 15 pounds of coloring matter per ton of seed. This coloring matter has been isolated, but is of little practical value. The loss in refining the crude oil is from 5 to 7 per cent. This is an extremely varying factor, depending on the percentage of free fatty acids and the proportion of coloring and albuminous matter present, or, briefly, on the character of the seed. The yield of oil depends on the soil, season, and skill of manufacture, and ranges from 35 to 42 gallons of crude oil per ton of seed.

14. Refining of Crude Cottonseed Oil.—In the refining process, the first step is to separate as quickly and as

thoroughly as possible the foreign matter from the expressed crude oil. The residue obtained on settling or filtration is known as *settlings* or *foots*. The precipitate, or residue obtained in the refining process is sometimes termed *soap stock* but is known in the cottonseed trade as *cottonseed foots*, under which name it is sold. (*Foots* is a loose term at best, and foots and soap stock are frequently used indiscriminately.) The crude oil freed from settlings is now pumped into the first-treatment tank, where it is agitated under increased temperature with caustic-soda lye of strength and proportion adapted to the quality of oil undergoing treatment. When sufficient time has elapsed for the complete absorption of the alkali, the agitation is ceased and the contents of the kettle is allowed to remain at rest. During this time the soap, which is formed by the combination of the free fatty acids with the caustic alkali and is contaminated with the organic impurities of the oil, settles to the bottom. The supernatant oil thus partly clarified is then transferred to the second-treatment tank, where it undergoes a bleaching process with fullers' earth. The proportion of fullers' earth used varies with the quality of the oil and may run from 2 to 5 per cent.; often a second treatment with fullers' earth after filtration is required.

The oil after agitation with fullers' earth, under increased temperature, is passed through the filter press. The filtrate constitutes the prime summer yellow cottonseed oil used in soap making. The various grades of edible and industrial cottonseed oils are obtained from this product by subsequent treatments with fullers' earth and filtration. The winter cottonseed oil used in miners' lamps requires limpidity at a low temperature. This condition is obtained by chilling the oil to a temperature below 0° C., whereby the so-called cottonseed-oil *stearin*, which is really palmitin, separates. This cottonseed stearin is used in the manufacture of oleomargarine, and of butter and lard substitutes.

15. Grades of Cottonseed Oil.—The requirements of the Texas Cottonseed Crushers' Association for the various grades of cottonseed oil compel a uniformity of quality that

is absent in the soap stock of animal origin. The summer yellow oil employed in soap manufacture is usually examined for color, moisture, free fatty acids, and titer, the last test being of chief importance in determining comparative value for the use of soap makers.

16. Crude Cottonseed Oil.—The following are rules of the Texas Cottonseed Crushers' Association relating to cottonseed oil:

Measurement.—A tank (tank car) of cottonseed oil shall be 125 barrels. A barrel of oil, if sold loose, shall contain 50 gallons. A gallon of oil shall weigh $7\frac{1}{2}$ pounds, avoirdupois.

Classification.—Crude cottonseed oil shall be classed and graded as follows:

Choice crude must be made from sound decorticated seed, must be sweet in flavor and odor, light in color, free from water and settlings, and test not over 1 per cent. of free fatty acids. It shall produce, when properly refined, choice summer yellow oil at a loss in weight not exceeding 6 per cent. for Texas oil, and at a normal loss for oil from all other parts of the country.

Prime Crude.—Crude cottonseed oil to pass as *prime* must be made from sound decorticated seed, must be sweet in flavor and odor, free from water and settlings, and must produce prime summer yellow grade by the usual refining methods with a normal loss in weight, provided the oil shall not be rejected for a nominal amount of settlings; but reasonable reduction shall be made in value for all such settlings in excess of $\frac{1}{4}$ per cent.

Off Oil.—All oil neither choice nor prime shall be called *off oil*, and shall be sold by sample.

17. Refined Cottonseed Oil.—According to the rules of this association, refined cottonseed oil shall be classed and graded as follows, summer yellow oil only being considered:

Choice summer yellow must be sweet in flavor and odor, of light straw color, clear and brilliant in appearance, free from moisture, and must bleach to a choice white.

Prime summer yellow must be clear, sweet in flavor and odor, and of yellow color, not reddish, and free from water and settlings.

Off Oil.—This grade consists of all oils having any objectionable flavor or odor, or that are of a reddish color.

18. Cottonseed Oil Soap Stock.—The precipitate obtained from the crude oil freed from settlings, on treatment with caustic-soda lye, consists of soap and free oil mixed with mucilaginous and coloring matters. This mixing

undergoes further treatment with caustic alkali, which transforms all the free oil into soap. The finished soap is grained, and is then subjected to further brine and alkali washings in order to obtain a product as free from odor and light in color as possible. After this stock has been suitably purified and is on the final settling, it is run while hot and in a semifluid condition into barrels.

19. Requirements of the Texas Cottonseed Crushers' Association for Soap Stock.—According to the requirements of the Texas Cottonseed Crushers' Association, all sales, unless otherwise agreed on by buyer and seller, are on a basis of 50 per cent. of fatty acid, not to fall below 40 per cent. If containing less than 40 per cent. of fatty acid, soap stock shall not be considered merchantable. Delivery is to be made in iron-bound hardwood packages or tank cars. A tank car of soap stock shall be 50,000 pounds for contract purposes.

20. Coconut Oil.—The fruit of the coco palm, the *Cocos nucifera* of the tropics, is the source of coconut oil. The oil is expressed from the pulp of the nut, which contains about 50 per cent. of oil. It occurs on the market in three general grades, namely, Cochin, Ceylon, and copra oil. The terms *Cochin* and *Ceylon* have reference to the geographical origin of the fruit.

Considerable coconut oil is produced in the West Indies and in the tropical parts of America. That from Trinidad compares very favorably in color, body, and odor with the Cochin grade; but that from Cuba is inferior in quality and yellowish in color, and therefore cannot be used for the better grades of bath and floating soaps. Cochin coconut oil is usually sufficiently superior in quality to command a price of from $\frac{1}{2}$ to 1 cent a pound more than Ceylon oil.

Cochin coconut oil is expressed from fruit grown in Cochin-China and adjacent territory, and on the islands of the China Sea.

Malabar and Manila oil is of good quality. Mauritius and the Fiji Islands also produce considerable. The coco palm is

a native of Cuba, and at one time oil crushing was a thriving industry on that island.

Ceylon coconut oil is a product of the island of Ceylon and of the adjacent regions. The different grades of coconut oil arise from the varying skill and the nature of the apparatus employed in its recovery, some of the apparatus being very crude. Where improved milling machinery has been introduced, coconut oil of uniform and superior quality is obtained; the greater part of the oil, however, is extracted by the most primitive methods. The oil arrives at the factory in immense casks, pipes, puncheons, and hogsheads containing from 800 to 2,000 pounds.

Copra coconut oil is made from the dried pulp or meat of the coconut, called *copra*. This pulp yields, on steaming and pressing, the lowest grade of coconut oil. The best oil of this grade is obtained from the ripest and most quickly pressed copra. Owing to its high percentage of the lower fatty acids and to its greater exposure, the copra oil is more liable to become rancid than is oil of the Ceylon and Cochin grades. The Ceylon and Cochin oils are expressed in the districts near the shipping ports, while copra is produced almost entirely in territory deficient in shipping facilities. Great quantities of copra are shipped to Marseilles, France, where the oil is expressed. In Sydney, New South Wales, copra crushing is a thriving industry.

21. Coconut oil is desirable as a soap stock because it contains a high glycerine yield and possesses distinct and peculiar qualities that define it sharply from all other animal and vegetable oils. In this connection, it may be well to note that there is no sharp distinction between a fat and an oil. Fat, which is usually of animal origin, is the term generally applied to the glycerides that are solid at ordinary temperatures; oil, on the other hand, may be of either animal or vegetable origin and is liquid at ordinary temperatures.

22. Palm-Kernel Oil.—In its chemical composition and behavior toward saponifying agents, palm-kernel oil is closely allied to coconut oil. While it is used extensively in

Europe, it finds only limited application in the United States as a soap stock. It is expressed from the kernel of the palm nut, the fleshy envelope of which is the source of palm oil. The oil is white and has an agreeable odor and taste, but on aging it becomes rancid. Oudemans gives the following as the approximate composition:

Clyceride	Per Cent.
Olein	26.6
Stearin, Palmitin, Myristin	33.0
Laurin, Caprin, Caprylin, Caproin	44.4

23. Palm Oil.—The fleshy part of the fruit of the palm tree, the *Elæis Guineensis* and the *Elæis melanococca*, native along the west coast of Africa, is the source of palm oil. According to its source and the mode of expressing it, palm oil is of butter-like to tallowy consistency, varying in color from orange to dark red, and possesses a characteristic violet-like odor.

The oil can be bleached by blowing air through it for a number of hours while the oil is maintained at a temperature of 80° to 90° C. But this can be accomplished better and more quickly by chemical bleaching, which destroys the odor as well as the color.

The chemical bleaching of palm oil is carried out in the following manner: After carefully removing all water and impurities by subsidence, the oil, cooled to a temperature of 105° to 110° F., is pumped into a lead-lined tank. While being constantly agitated by air, $\frac{3}{4}$ of 1 per cent. of bichromate of soda dissolved in the least possible amount of water is run in, followed by $1\frac{1}{2}$ per cent. of hydrochloric acid and $\frac{1}{4}$ per cent. of sulphuric acid. At the end of 20 minutes the bleaching will be finished, and the acids and oxide of chromium are removed by allowing 25 per cent. of hot water to run

in. It is preferable to allow the contents of the tank to remain undisturbed over night and to remove the clear oil in the morning.

The *Lagos oil* is the best quality made; it is of a deep, reddish-orange color and contains free fatty acids averaging from 20 to 30 per cent. The common grades of palm oil are yellow in color, and on account of the primitive methods employed in extracting them, the free fatty acids are very high, running from 50 to 80 per cent. Deductions for moisture, dirt, and impurities are allowed on sales made, provided they amount to over 2 per cent., which is generally the case.

Since the titer of palm oil is very uniform, never varying much from 44° to 45° C., the chief industrial chemical tests made are the determinations of the impurities and of the free fatty acids present.

24. Corn Oil.—The germ obtained as a by-product in the manufacture of starch and glucose from maize is utilized in expressing corn oil. This oil is closely allied to cottonseed oil in its soap-making properties. It is usually of a bright-yellow color, but may be bleached with fullers' earth to whiteness, as is done with certain edible grades of cottonseed oil.

In the manufacture of the oil, the corn is first steeped in water, so as to loosen the hull from the grain, which becomes swollen and tough from the absorption of water. The steeped kernel is then passed between rollers to separate the envelope and the starch from the softened germ, which remains whole and of the size of a grain of rice. The crushed corn is then transferred to tanks filled with water, in which the crushed grains sink, leaving the germs to float on the surface. These are removed, cooked, and compressed for the oil.

On account of its higher titer, from 33° to 35° C., cottonseed oil as a soap stock is much to be preferred to corn oil, the titer of whose fatty acids ranges from 17° to 19° C. Corn oil mixed with other stocks is used quite extensively in the production of soaps of soft body, to be used in the manufacture of soap powders. This mixture gives a soap readily

soluble in cold or lukewarm water, a characteristic very essential to a good powder.

25. Olive Oil.—The pulp, or fleshy portion, of the fruit of the oilve tree, the *Olea Europæa*, native in the Mediterranean countries, is used for making olive oil. In these countries, olive oil has been employed from the earliest time as the fatty base of Castile soap. The use of olive oil for this purpose has of late years been largely displaced by the cheaper cottonseed oil, large quantities of the latter being exported from the United States to Marseilles for this purpose. Olive oil is used chiefly as an edible oil, and inferior grades only are used in the soap kettle. Olive oil finds very limited use as a soap stock in the United States. It contains about 72 per cent. of olein and 28 per cent. of palmitin, and behaves like cottonseed oil toward saponifying agents.

In the manufacture of olive oil, about 10 bushels of olives is crushed at a time in an edge-stone mill. The pasty mass that results, consisting of pulp and stones, is then placed in filter cloths and subjected to hydraulic pressure. The first pressing of the olives yields the finest oil. After the first pressing, which yields the virgin oil, as it is sometimes called, the press cake is ground up with water in the edge-stone mill, and the paste is then subjected to a second pressing. The second pressing yields an oil of inferior quality. The press cake after the second pressing still contains a large quantity of oil which, when recovered, constitutes the olive-oil foots of commerce. Table II shows the specific gravity, weight per gallon, etc. of the principal fatty oils.

26. Olive-Oil Foots.—The oil remaining in the press cake after the second pressing may be extracted in either of two ways, but when recovered it is of such inferior quality as to be suitable only for industrial purposes. It is fairly fluid, dark green to black in color, and has a disagreeable odor. Its inferiority results from being contaminated by the green coloring matter and pulp of the fruit. To recover the remaining oil, the press cake is first well ground, hot water being added during the process. The dark pasty mass is

then transferred to a tank and agitated with water until the broken olive stones drop, free from pulp, to the bottom of the tank. The oily residuum floating on the surface of the water is then transferred to another tank, where the free oil is removed. The pulp residuum is again pressed and yields some oil. Olive-oil foots obtained in this manner are said to be *washed*.

The press cake may also be extracted with a volatile solvent, carbon disulphide or naptha being commonly used.

TABLE II

SPECIFIC GRAVITY OF FATTY OILS AT 15° C. (60° F.)

Name of Oil	Specific Gravity
Almond oil	.918–.919
Arachic (peanut) oil	.917–.920
Castor oil	.959–.967
Coconut oil	.924–.926
Corn oil	.921–.922
Cottonseed oil	.923–.925
Lard oil	.912–.915
Linseed oil	.932–.936
Neatsfoot oil	.914–.917
Olive oil	.916–.918
Palm oil	.943–.946
Palm-kernel oil	.9119 (at 40° C.)
Rape oil	.913–.917
Sesame oil	.924–.926
Tallow oil	.910–.912
Tallow	.943–.952

The broken press cake is agitated with the solvent, after which the solution thus obtained is transferred to a covered tank. Here the solvent is distilled off and collected for subsequent use, leaving the recovered oil behind. This oil is black and retains the odor characteristic of the solvent. It is inferior to *washed* foots. This process, however, possesses the advantage of extracting the oil completely.

Soap made from olive-oil foots retains the green color of the recovered oil; the color, however, gradually bleaches out on exposure.

27. Red Oil.—In the manufacture of candles, a by-product known as red oil is obtained. This oil consists almost wholly of oleic acid, and derives its name from the color that it acquires on aging. The color, however, is chiefly due to contact with the iron. Sometimes this color is developed by the use of dyes and sometimes by chemical treatment with sulphur or nitric oxide. Red oil occurs in two grades, namely, saponified and distilled red oil.

Saponified red oil is obtained by either acid, lime, or aqueous saponification under pressure, in specially constructed tanks called autoclaves, or digesters. The mixed fatty acids resulting from saponification are resolved roughly into stearic and oleic acids by pressure through filter cloths. The stearic acid still remaining in the liquid portion is separated by chilling, whereby the commercial oleic acid, or red oil, is obtained.

Distilled red oil is obtained by distilling the mixed fatty acids with steam. By means of the process of fractional condensation, fatty acids of different melting points are separated. Distilled red oil varies in its composition according to the method employed in its manufacture. The following are analyses of two samples of commercial oleic acid:

Ingredients	Sample A Per Cent.	Sample B Per Cent.
Color	Pale	Brown
Oleic acid	93.06	87.70
Oil	6.04	9.41
Hydrocarbons	.90	2.89
Total	100.00	100.00
Specific gravity	.897	.904
Turbid at	42° F.	38° F.

Red oil is a valuable soap stock. It admits of a nearly complete saponification with soda ash, as will be fully explained elsewhere.

28. Manufacture of Saponified Red Oil.—Saponified red oil, as just stated, may be obtained by three methods of saponification, namely: lime saponification, acid saponification, and aqueous saponification.

29. Lime-Saponification Process.—The digester, or autoclave, used in the lime-saponification process, is a strongly built tank, usually of copper, although some are made of iron, from 3 to 5 feet in diameter and from 18 to 25 feet in height. The digester may be set up either horizontally or vertically. It is covered with an asbestos jacket, to retain the heat, and is provided with a safety valve, a cock for the removal of samples, and a pressure gauge. At one end are located pipes for the introduction of the tallow and lime, for the discharge of the contents of the digester after saponification, and for the introduction of live steam.

The tallow is previously purified, if required, by boiling in weak brine and then allowing the impurities to subside. The brine wash is then run off, and the tallow is maintained in a fluid state by means of a closed steam coil. The quantity of unslaked lime commonly used for saponification is from 2 to 4 per cent. of the weight of the tallow. Both the tallow and lime tanks are on an elevation above the digester, and after the lime has been thoroughly mixed with water and the tallow melted, they are allowed to run by gravity into the digester. The charging of the digester may be hastened by creating a partial vacuum in it by the condensation of steam previous to running in the charge.

After the charge has been added, steam is turned on and maintained at a pressure of from 8 to 10 atmospheres for a period of from 4 to 10 hours, or until the saponification is complete; 8.7 per cent. of lime is theoretically required, but under the conditions maintained in the digester, from 2 to 4 per cent. has been found to be sufficient in practice. Samples are removed from time to time and tested for unsaponified matter. On completion of saponification, the contents of the disgester is blown into wooden tanks, or vats, situated above the digester.

The mass resolves itself into two layers: the supernatant lime *rock*, consisting of lime soap and fatty acids, and the *sweet* water, in which is dissolved the glycerine liberated from the stock. The glycerine solution is now allowed to flow by gravity to the glycerine plant, while the lime rock is again boiled up with water and live steam in order to remove the last traces of glycerine. This wash liquor is removed as before.

The decomposition of the lime rock is effected by adding slowly, under constant agitation, the calculated quantity of dilute sulphuric acid. The fatty acids of the lime soap are thus set free. The mass at once resolves itself into two layers: the supernatant layer, consisting of the total fatty acids, and the water containing the calcium sulphate in solution and as a precipitate. The acid liquor and precipitate are now discharged into the sewer, and the fatty acids are washed free from all traces of sulphuric acid.

30. Acid-Saponification Process.—In Fig. 2 is shown a type of apparatus of English manufacture employed in the acid-saponification process for the manufacture of fatty acids for candle stock.

The raw material, whether it be tallow, palm oil, recovered grease, or any fatty body containing stearin, is first melted in the tank marked *A* and is then transferred to the storage tanks *G*. These tanks are wooden and lead-lined and are provided with acid-resisting steam coils. In these storage tanks the fat undergoes a preliminary purification, as already briefly described. The mass is then transferred to the acidifier marked *D*. It is there treated with from 4 to 12 per cent. of concentrated sulphuric acid, which is introduced by gravity from a tank *E* located immediately above. In the acidifier *D*, the mixture is subjected to the action of superheated steam furnished by the superheater *F*. To condense the acrid vapors evolved during the reaction, a jet condenser provides a slight vacuum in the acidifier, and the vapors are thus drawn over and discharged into the reservoir *d*.

After the acidification is complete, the material is discharged into the storage tanks *G*, where the acid liquor is

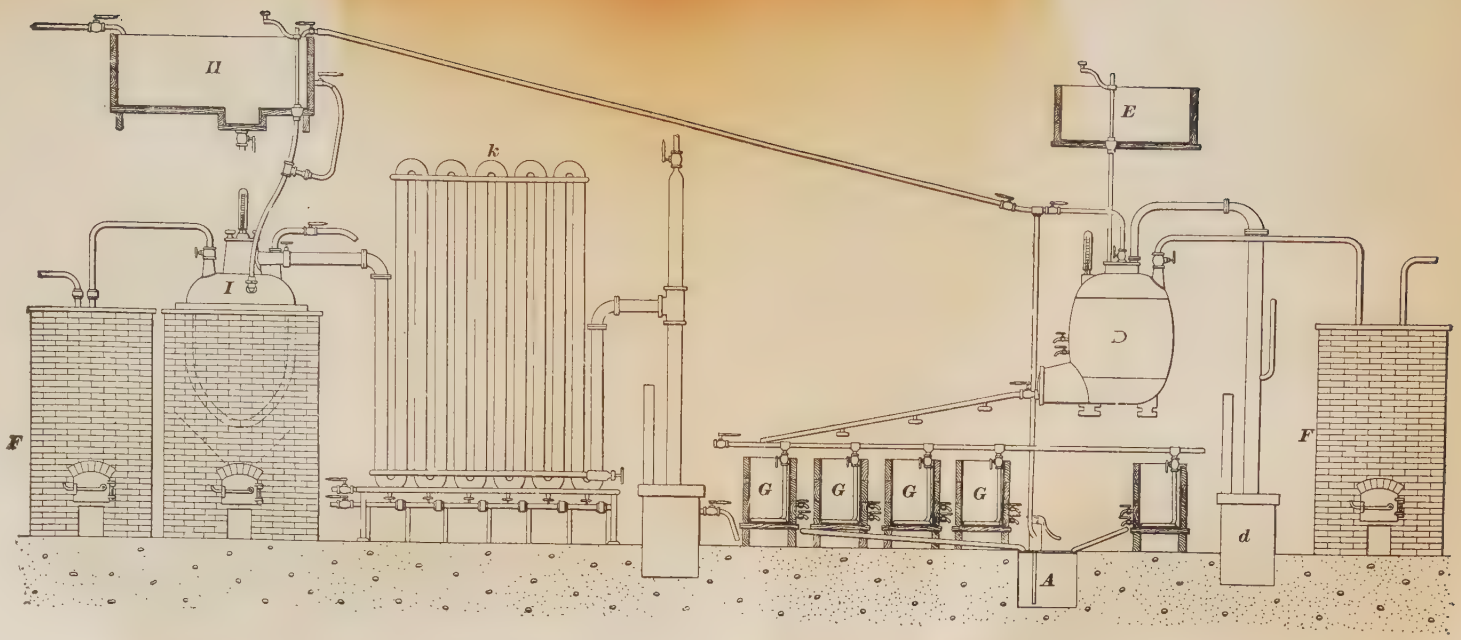


Fig. 2

removed and the fatty acids are washed free from all traces of sulphuric acid.

31. Aqueous-Saponification Process.—Many establishments manufacturing candle stock employ neither acid nor lime in the hydrolysis of the glyceride, but saponify their tallow, bone fat, or other stock merely in the presence of water and a catalyst under a steam pressure of 150 pounds. These catalysts, or *saponifiers*, are usually made by the action of sulphuric acid on a solution of oleic acid in an aromatic hydrocarbon. This hydrocarbon may be benzene, toluol, or naphthalene. Higher alcohols have also been successfully employed, such as phenol and cetyl alcohol. It can readily be seen how a sulphonated product is obtained which in the case of benzene corresponds to $C_6H_4(SO_3H)C_{18}H_{35}O_2$. It requires from 1 to $2\frac{1}{2}$ per cent. of the saponifier for the reaction, which proceeds best when the fat or oil contains a little free fatty acid of its own. This is called the autoclave process. Saponification by means of water is the simplest and most convenient of the three processes described, inasmuch as the lime and acid treatments are made unnecessary. The process otherwise is carried on in precisely the same manner as described in the lime-saponification method.

32. Twitchell Process.—A process for the separation of the fats and oils into fatty acid and glycerine has been worked out by Twitchell. This process differs from similar processes in that he employs a saponifier. This saponifier is made by allowing sulphuric acid to act on oleic acid in the pressure of an aromatic hydrocarbon, benzene or naphthalene. When benzene is used the formula for the saponifier may be expressed as $C_6H_4(SO_3H)C_{18}H_{35}O_2$.

The process requires that the original fat or oil be purified by boiling with dilute sulphuric acid. It is then mixed with an equal amount of distilled water and $1\frac{1}{2}$ to 2 per cent. of the saponifiers and boiled in wooden tanks, fitted with brass coils and a tight cover. Any access of air tends to darken the fatty acid and this has been one of its chief drawbacks.

The Twitchell product often has to be distilled to get light-colored fatty acids. It has not found great favor with the soapmakers as yet.

33. Distillation of the Fatty Acids.—The fatty acids, whether obtained by the lime, acid, or aqueous saponification, are subjected to the same process of distillation. When made of pure and fresh raw material, the resulting fatty acids are of sufficiently good color to press immediately. The dark-colored fatty acids before pressing are subjected to distillation with superheated steam. Referring to Fig. 2, the fatty acids are pumped to the charging tank *H* situated on an elevation above the still *I*, into which these acids may flow by gravity. The still, generally of copper or copper-lined, is of variable capacity. A still of ordinary size will accommodate from 16,000 to 18,000 pounds at a *run*, during which the volume of material in the still is kept constant by the addition of fatty acids from the charging tank above. As shown in Fig. 2, the still is incased in brickwork and is heated externally by fire and within by superheated steam, which passes through copper coils from the superheater *F*. The products of distillation are condensed in the vertical cooling tubes *k*, which connect at the bottom with coils immersed in warm water. The condensed fatty acids are here melted, to admit of their easy removal. The distillate is commonly collected in three fractions, namely, the first-run oil, comprising three-fourths of the total charge; the second-run oil, which is returned to the charging tank and redistilled with the next run; and the final portion, called from its color *green oil*. The residue in the still is known as *candle tar*.

34. Pressing the Fatty Acids.—The fatty acids, whether having been subjected to a previous distillation or used directly from the autoclave, are transferred to square, shallow pans, or trays, supported on shelves in the granulating room. These trays are of enameled iron and are so placed that each tray, beginning at the end, is at a higher elevation and slightly over the succeeding one. It is thus possible to

fill every pan in the series by running the melted fatty acids into the topmost, which, when full, overflows into the succeeding one, and so on until all are filled. Were the fatty acids cooled rapidly, the crystals of the fatty acids of different melting points would be so closely interlocked that the oleic acid could not be readily separated from the stearic. By allowing the mixture of fatty acids to cool slowly for a period of from 2 to 3 days in the granulating room, at a temperature of about 80° F., the stearic acid crystallizes in a menstruum of the liquid oleic acid. There is thus obtained at the expiration of this stage of the process a cake of stearic acid colored brown by the oleic acid.

The pan is now inverted on a woolen or a camel's-hair cloth, on which the cake falls. When the required number of cloths have been filled they are transferred to the hydraulic press. Each cloth with its contents is separated by an iron plate. Pressure is applied very gradually at first, whereupon the crude oleic acid, or red oil, is expressed. The oil is then conducted to storage tanks, from which it either is run to the department in which it is used or is barreled for shipment.

The first pressing separates about 50 per cent. of the oleic acid present and is done cold. The cakes thus obtained are subjected to a second pressing between hollow iron plates heated with steam. The hot pressing is effected in a horizontal hydraulic press. The stearic acid now obtained is of snowy-white appearance and very hard and brittle. It melts at 52° to 55° C. and is ready for the candle manufacturer.

35. Comparison of the Processes for the Manufacture of Fatty Acids.—The yield of solid fatty acids from tallow by lime saponification is from 44 to 48 per cent. Aqueous saponification admits of a slightly higher yield, namely, 50 per cent., from the same raw material; acid saponification yields upwards of 55 per cent. of fatty acids. It is found in practice that distilled stock yields a press cake of lower melting point than that obtained from fatty acids used directly from the autoclave. This fact taken together with the greater yield of the acid-saponification process with which

process distillation is used may be explained by the polymerizing action of the sulphuric acid on the oleic acid in the still, whereby a body is formed of sufficient firmness to resist being expelled from the press cake with the crude oleic acid, and thus remains to lower the melting point and to add to the yield.

With lime saponification, practically all the glycerine, upwards to 10 per cent., is obtained; with the acid saponification, not more than 3 per cent. is recovered. If it is desired to recover as much glycerine as is possible, in addition to the solid fatty acids, the lime saponification is preferable. If fatty acids are the sole desideratum, the distillation process is better.

36. Rosin.—The solid residue left on the distillation of crude turpentine is rosin. The rosin, or crude turpentine, exudes from the pine tree, chiefly the longleaf yellow pine of the Southeastern Atlantic and Gulf States. This rosin is of whitish color and of semisolid consistency. A number of deep incisions are made in the trunk of the tree starting about 1 foot from the ground, and each incision, or *box* holds about a quart of the crude rosin. The number of boxes cut in each tree, depends on the size of the tree. As the season advances, the flow of rosin is increased by removing the bark and wood to the depth of 1 inch above the box. At regular intervals, the exuded rosin is collected and distilled.

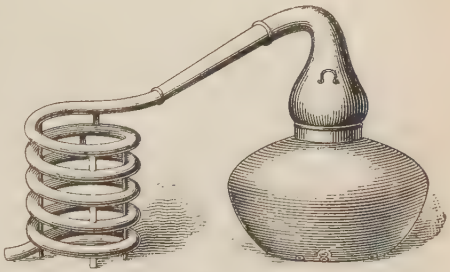


Fig. 3

The still (see Fig. 3) used for distilling rosin is made of copper and varies in capacity from 10 to 50 barrels of crude turpentine. It is mounted on brickwork and has a furnace underneath. After the still has been charged, some water is run in and the contents is heated. The fire is increased

gradually until the contents of the still has reached the boiling point, which temperature is maintained until practically all the volatile matter has been distilled over. As the distillation proceeds, water is added from time to time so as to replace that lost by evaporation and to prevent the product from being darkened by incipient burning. The distillate, separated from the water that has distilled over with it, constitutes the oil of turpentine of commerce. The hot liquid residuum in the still is now discharged through a valve near the bottom, strained through sieves of increasing mesh up to No. 80, usually three in number, and is finally run into barrels. A charge of 12 barrels of crude turpentine, weighing upwards of 4,500 pounds, will yield on distillation about 3,600 pounds of rosin and about 900 pounds of oil of turpentine.

37. The gross weight of a barrel of rosin is about 500 pounds and the net weight averages 420 pounds, the barrel itself always being paid for at the same rate as the rosin. Rosin is marketed on a basis of 280 pounds to a barrel, and according to law, the empty barrel may weigh 15 per cent. of the weight of the barrel when filled. This is equivalent to 40 pounds for Alabama and 70 pounds for Savannah cooperage.

Opaque rosins contain turpentine and water, and when used in soaps they affect the hardness to a certain extent; that is, the soaps become soft in very hot weather.

There are about fifteen grades of rosin, varying in color from *water white*, which is clear and almost colorless, to the lowest grade, commercially known as "C. A.," which is black. The various qualities arise from the length of time during which the crude rosin is collected from a single *camp*.

The first year's run furnishes the best grades, while with each succeeding year a more inferior grade is obtained. The following grades are used in the soap industry:

W. W., or Water White.
W. G., or Window Glass
N., or Extra Pale
M., or Pale.
K., or Low Pale.

Most of the rosin used for soap making is of the M and N grades.

Rosin is graded by sample, a $\frac{7}{8}$-inch cube being cut from the head of each barrel. Uniformity of size is important, as the thickness of the cube determines the shade of color, and therefore the value. Those who buy and sell rosin are provided with sample cubes representing the quality of the standard grades. The determination of the quality of a shipment, therefore, is simply a matter of comparing the sample cubes with those of the standard grades.

38. Rosin is acid in its composition, consisting of the anhydrides of the so-called rosin acids. Like red oil, rosin can be almost entirely saponified with soda ash. The alkaline salts of the rosin acids, while not constituting a true soap, possess marked detergent properties and are a valuable ingredient of household soap. The English were the first manufacturers of rosined soaps.

As rosin decreases in quality from the brighter to the darker grades, the percentage of unsaponifiable matter increases, as is indicated by the following determinations of the unsaponifiable matter:

Marks	Percentage Unsaponifiable Matter
W. W.	3.07
W. G.	3.88
N.	4.08
M.	6.34
K.	6.62

The coloring matter present in rosin is the cause of the high color of the waste soap lye withdrawn after the rosin change in the manufacture of settled rosin soap.

ALKALIES AND THEIR MANUFACTURE

39. Soda Ash, or Sodium Carbonate.—All the commercial sodium compounds start from common salt as a raw material. Before the development of the Le Blanc process, potash was used exclusively as the saponifying agent in the primitive soap manufacture of those days. The potash was obtained by burning sea-weeds and lixiviating the ashes. The solution thus obtained was then causticized with quicklime. During the embargoes of the French Revolution, the supply of potash was cut off from France. As the result of a prize offered by the French government for a practical method of manufacturing soda ash from common salt, the Le Blanc process was given to the world. So perfectly was this process outlined in its original specifications that it has undergone no change in its essential principles in its entire history.

40. The Le Blanc Process for the Manufacture of Sodium Carbonate.—The manufacture of soda ash, or sodium carbonate, Na_2CO_3, from common salt by the Le Blanc process is carried on practically in three stages, as expressed in the following reactions:

1. Common salt, or sodium chloride, is converted into sodium sulphate by treatment with sulphuric acid.

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl$$

The hydrochloric-acid gas is absorbed by passing it through towers down which water is allowed to trickle. The aqueous solution of the gas thus obtained constitutes the muriatic acid of commerce.

2. The sodium sulphate obtained by the preceding reaction is mixed with coal and fused in specially constructed furnaces. The coal reduces the sulphate to sulphide.

$$Na_2SO_4+2C=Na_2S+2CO_2$$

3. The sodium sulphide is now heated with carbonate of lime, which then reacts to form calcium sulphide and sodium carbonate.

$$Na_2S+CaCO_3=CaS+Na_2CO_3$$

The product of this reaction is crude soda, or black ash. The fused mass is allowed to cool and then broken into fragments and lixiviated with water. The sodium carbonate in solution is allowed to crystallize out as $Na_2CO_3 \cdot 10H_2O$. The water of crystallization is expelled by heat, leaving the sodium carbonate or soda ash of commerce.

41. The Le Blanc process, although a creation of French ingenuity, enjoyed its greatest development on English soil, and for half a century was one of the chief mainstays of England's industrial supremacy. The practical employment of the process involved certain technical and many unsanitary disadvantages, whose baneful effects proved a constant encouragement for the development of a simpler and more hygienic process. The mechanical difficulties surrounding the production of alkali by what is now known as the *ammonia process* met their first practical solution at the hands of Ernest and Alfred Solvay, and in the past 35 years works operating the process originally covered by the Solvay patents have been established in every civilized country. The first ammonia-soda works were established in Belgium in 1863. Later, immense works were established in England by Brunner, Mond & Co., whose name is closely associated with the development of the process in Great Britain.

The Le Blanc process has received the most thorough scrutiny of the best scientific minds, and the efforts made to enable it to survive in the face of the more economical production of a competing process have resulted in the most complete economy of operation. As a remunerative producer of alkali, the ammonia process early displaced it, with the result that the process is dependent for its profits entirely on its chlorine products. As yet no economical production of bleaching powder from the calcium-chloride waste of the ammonia-soda process has been wrought out on an extensive commercial scale, and as these two rival chemical processes stand today, the Le Blanc has command of the chlorine industry, while the scepter of remunerative alkali production has passed to the ammonia process.

42. Solvay, or Ammonia-Soda, Process.—The Solvay process for the production of soda ash from common salt is based on the precipitation of sodium bicarbonate in an ammoniacal solution of common salt by means of carbonic-acid gas. Practically all soda ash now produced is obtained by this process.

In the practical operation of the Solvay process, the employment of labor is reduced to a minimum. The materials employed in the direct manufacturing processes are either in a gaseous state or in aqueous solution. The fundamental chemical reaction of the process is as follows:

$$NaCl+NH_3+H_2O+CO_2=NH_4Cl+NaHCO_3$$

The salt is dissolved in water to form a very pure and concentrated brine. It is then saturated with ammonia gas. The liquor thus formed is introduced under pressure into the *carbonating* tower at a distance about one-third from the top. The carbonating tower is upwards of 65 feet in height and is made of up of segments about 3.5 feet high and 6 feet in diameter. The carbonic-acid gas is forced into the tower through the bottom segment and is made to ascend in bubbles by means of a perforated plate covering a hole in the bottom of each segment. The reaction indicated by the preceding formula takes place in the carbonating tower. The success of the ammonia-soda process depends on the insolubility of the sodium bicarbonate in a cold, ammoniacal solution of common salt. The heat produced by the chemical reaction is taken up by cold water circulating in cooling pipes placed in each segment of the carbonating tower.

43. As the reaction proceeds, the precipitated sodium bicarbonate accumulates in the bottom of the tower, from which place it is withdrawn from time to time as a thick, milky liquid, containing ammonium chloride and sodium chloride in solution and the sodium bicarbonate in suspension. The solid bicarbonate is separated from the chlorides of ammonium and sodium in solution by means of centrifugal machines, and it is then washed with water to remove traces of these impurities. The bicarbonate is then calcined to

form a normal carbonate in accordance with the following reaction:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

The Solvay soda ash thus obtained has a specific gravity of only .8, owing to its extremely finely divided condition. To increase the ease of handling this soda ash and to bring it up to the density of Le Blanc soda ash, namely, 1.2, it is made more compact by subjecting it to a second ignition. It is then ground and packed in bags and casks for shipment. Soda ash made by this process is much purer than the Le Blanc soda ash. It contains only traces of salt and bicarbonate and is free from the sulphide, sulphate, and hydrate of sodium.

44. Caustic-Soda Manufacture.—The manufacture of caustic soda is based on the following reaction:

$$\underset{106}{Na_2CO_3} + \underset{74}{Ca(OH)_2} = \underset{80}{2NaOH} + \underset{100}{CaCO_3}$$

According to this reaction, 100 pounds of sodium carbonate will yield on causticization 75.4 pounds of sodium hydrate. In the manufacture of caustic soda from the soda ash of the Le Blanc process, the lime is added to the solution obtained by lixiviating the black ash. The solution must not have a density in excess of 13° Baumé, or a reversion of the calcium carbonate will result. The impure solution of sodium carbonate is therefore diluted, if necessary, and the *milk of lime* added. Under heating and agitation with air, the reaction represented by the preceding formula takes place. Zinc oxide is added to reduce the sodium sulphide; thus,

$$Na_2S + ZnO + H_2O = 2NaOH + ZnS$$

The addition of sodium nitrate, together with the air used for agitation, suffices to oxidize any thiosulphate to the normal sulphate. The solution is then allowed to settle, and the supernatant solution of caustic soda is removed and evaporated until a density of 33.5° Baumé is attained, at which point most salts present as impurities crystallize out. The solution is then transferred to a heavy cast-iron pan, and the evaporation is continued over fire until all water is expelled and the caustic soda remains as a fused mass.

A sample representing the contents of the kettle is tested for total alkali. If found to be below 60 per cent. in quality, the contents is worked up to that test. If the test indicates the quality to be above 70 per cent., the product may be worked into the highest grade or into that grade testing most closely to the contents of the kettle. The reduction of quality to the grade of caustic desired is effected by the addition of salt. The fused caustic soda is then run directly into sheet-iron drums and sealed to prevent exposure to the atmosphere. Owing to the greater purity of the solutions, purer caustic soda can be more easily obtained from the Solvay process soda ash than from Le Blanc soda ash. In the case of Solvay soda ash it is not necessary to remove the impurities always characteristic of the commercial products of the Le Blanc process.

45. Although the production of caustic lye from soda ash by the soap maker may be effected at nominal cost, the use of the solid caustic, aside from other considerations peculiar to each works that may determine the installation of a causticizing plant, possesses superior advantages regarding cleanliness and convenience of working. The commercial production of solid caustic dates from 1854, at which time improvements introduced in its manufacture by William Gossage, in England, resulted in its more general use, although in a very impure state, by soap manufacturers and paper makers. Artificial alkali was first used in the manufacture of soap in 1823. It was manufactured in England by James Muspratt and according to the Le Blanc process. The Lancashire soap boilers were loath to accept this new and purer article, and it was only after Muspratt had distributed gratis scores of tons of Le Blanc soda that they became convinced of the superior economy of artificial over natural soda. The use of the sheet-iron drums was introduced by Thompson in 1857, this innovation being a most welcome improvement over cooling the liquid caustic on iron slabs and subsequently breaking it into pieces and packing in barrels for shipment.

46. Causticization of Soda Ash in the Soap Factory. The causticizing plant consists essentially of a converting

kettle, in which the chemical reaction indicated in Art. 44 is carried out, and a filter for the separation of the *lime mud.* The causticizing plant is shown in its essential characteristics in Fig. 4. It is required to causticize the soda ash as completely as possible, and for this reason the lime should be free from impurities. In causticizing a ton of soda ash, lime containing 2 per cent. of calcium sulphate will convert 42 pounds of a ton of soda ash into the less valuable product, sodium sulphate.

The solution of the soda ash in water is effected in the converting kettle *a* with the aid of live steam introduced

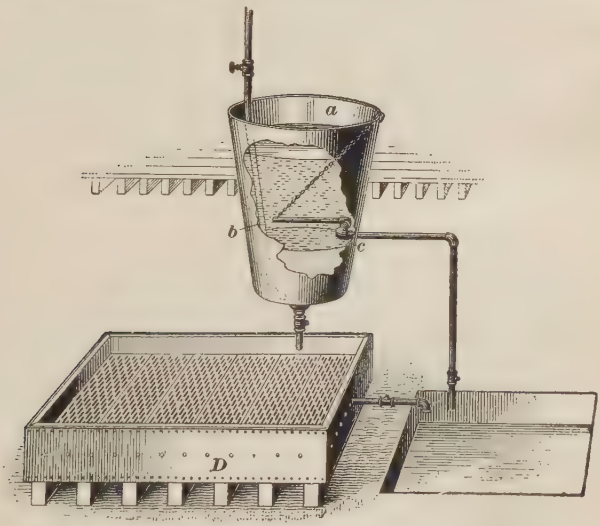


FIG. 4

through the pipe *b*, and the required amount of lime is shoveled in. The contents of the kettle is thoroughly agitated and boiled up with live steam, after which it is allowed to settle. The supernatant liquor is then pumped off through the swing-joint pipe *c*. The lime precipitate, or mud, is boiled up with water and dropped on the filter *D*, where it is drained and washed. In some instances this lime waste, known as *whiting*, is recovered. This product is utilized in the manufacture of putty and in the paper industry as a make-weight, or filler.

47. As shown by experiments carried out by Lunge, the results of which are given in Table III, the causticization is most complete with dilute solutions of soda ash.

It is claimed for the apparatus shown in Fig. 4 that a caustic-soda solution of 14.5° Baumé, equivalent to 600 pounds of 77-per-cent. caustic, can be obtained from 800 pounds of 58-per-cent. soda ash and 650 pounds of lime. As a solution of caustic soda of this density is too dilute when soap is boiled on open steam, evaporation of the weak

TABLE III

COMPLETENESS OF CAUSTICIZATION OF SOLUTIONS OF SODA ASH OF VARIOUS STRENGTHS (LUNGE)

Per Cent. Na_2CO_3 in Liquor	Specific Gravity Before Causticizing	Per Cent. Na_2CO_3 Made Caustic by Treatment	
		Test No. 1	Test No. 2
2	1.022 at 15° C.	99.4	99.3
5	1.052 at 15° C.	99.0	99.2
10	1.107 at 15° C.	97.2	97.4
12	1.127 at 15° C.	96.8	96.2
14	1.150 at 15° C.	94.5	95.4
16	1.169 at 30° C.	93.7	94.0
20	1.215 at 30° C.	90.7	91.0

caustic lye to the required density is resorted to when the facilities of the factory permit.

48. Electrolytic Production of Caustic Soda.—It has been long known that when a current of electricity is passed through a solution of sodium chloride the same is decomposed into its positive and negative ions, appearing, respectively, at the negative and positive poles, or, as they are called, the cathode and the anode.

When a solution of sodium chloride is thus electrolyzed, chlorine will appear at the anode and sodium at the cathode. Chlorine, being gaseous, will either pass into solution or be discharged into the atmosphere; sodium, being a very active

element, immediately decomposes the water surrounding the cathode, forming sodium hydrate and liberating hydrogen. Many varieties of electrolytic cells have been designed, with varying degrees of success, to serve as a commercial producer of caustic soda and chlorine. The chief mechanical difficulty in the production of a satisfactory electrolytic cell lies in the character of the diaphragm, which serves to separate the products liberated from the positive and negative poles. Chlorine must not be allowed to diffuse through the brine, as secondary reactions are set up. The problem is to find a satisfactory medium that will prevent the diffusion of the liberated products and at the same time offer no resistance to the passage of the electric current.

49. Castner Electrolytic Process for the Production of Caustic Soda and Chlorine.—In the Castner

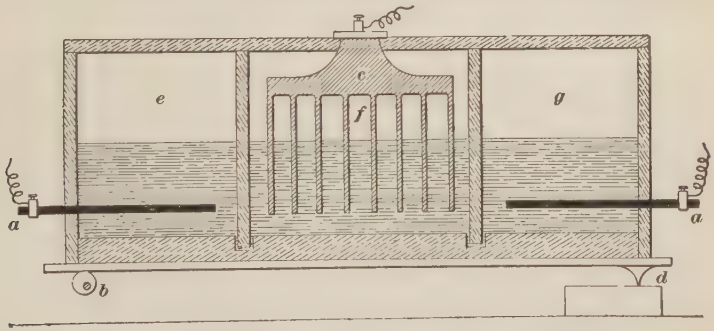


Fig. 5

cell, mercury is used to separate the chlorine liberated at the positive pole, or anode, and the sodium liberated at the negative pole, or cathode. The cell, as shown in Fig. 5, is essentially a box made of slate slabs and divided into three compartments marked *e*, *f*, *g*. Compartments *e* and *g* contain the salt solution and the carbon anodes *a*, while compartment *f* contains the caustic-soda solution and the iron cathode *c*. Sufficient mercury covers the bottom of the cell to alloy with the sodium as it is liberated. By means of the cam *b* the cell is subjected to a slight oscillation on the pivot *d*.

In this manner, the sodium-mercury amalgam is carried into compartment *f*, where the amalgam acts as the anode to the iron cathode *c*, the sodium being set free to combine with the water in compartment *f*. The electrolysis of the brine takes place in compartments *e* and *g*. The sodium immediately alloys with the mercury, which serves to carry the alkali into compartment *f*, where the formation of caustic soda takes place. A regulated supply of water is run into the middle compartment to combine with the sodium, which is allowed to flow out as a dilute caustic-soda solution in corresponding volume. The chlorine gas is removed by exhaustion from compartments *e* and *g*.

The Castner process is employed industrially at Niagara Falls for the production of caustic soda and bleaching powder, and appears to be one of the most successful devices of its kind that has yet been developed.

50. Comparison of the Methods of Alkali Manufacture.—The Le Blanc process for the manufacture of commercial alkali products is able to survive in the face of the cheaper Solvay process with its absence of waste products only by virtue of its production of hydrochloric-acid gas as a by-product.

So long as no cheaper method for the manufacture of muriatic acid is developed, the Le Blanc process will continue to be an important industry. In other respects, the Solvay process possesses every advantage.

The several electrolytic processes that have taken practical shape during the past few years have assumed a productive importance that will increase with each succeeding year. The problem of their commercial success is being gradually brought to a satisfactory solution, and what influence they may exert on the firmly established chemical processes is being watched with no little interest. As a producer of alkali, it is not likely that the ammonia process will be assailed. The older chemical process, which has so long monopolized the manufacture of bleaching powder, has most to fear from the growth of the electrolytic methods.

To sum up the essential differences between the chemical and electrolytic methods for the production of sodium compounds, it may be stated that the electrolytic process is direct, clean, labor saving, and free from worthless by-products. On the other hand, its units of plant are small, troublesome, expensive, and rapidly deteriorate with use. The chemical process provides a large output with comparatively few large units of plant of rather simple construction. The repairs, though costly, are not numerous and do not have to be applied to a vast number of small pieces of apparatus. To the disadvantage of the chemical process, it may be said to be arduous and that fairly skilled labor is required for its operation; also that a number of by-products, invariably troublesome and of little or no value, are produced.

51. Grading of Soda Ash.—The system of grading soda ash and caustic soda is based on the molecular composition of these bodies. The quotations of the various grades in terms, respectively, of 48-per-cent. alkali and 60-per-cent. caustic is handed down from the early Le Blanc days and is an evidence of the highest grades of those products they were then able to produce mechanically. The molecular weight of sodium carbonate, Na_2CO_3, is 106, composed of 62 parts by weight, or 58.49 per cent., of Na_2O, the remainder being CO_2. A soda ash that contains 58.49 per cent. of Na_2O is therefore chemically pure, this percentage being equivalent to 100 per cent. of Na_2CO_3. A 58-per-cent. alkali should contain 58 per cent. of Na_2O or its equivalent, 99.16 per cent. of Na_2CO_3; likewise, a 48 per-cent. alkali should contain 48 per cent. of Na_2O or its equivalent, 82 per cent. of Na_2CO_3. The reduction of any grade of soda to that of 48 per cent. is effected by admixture with common salt. Following are presented for comparison two fairly representative analyses of these two standard grades of soda ash:

Grade Per Cent.	Per Cent. Na_2CO_3	Per Cent. $NaCl$	Per Cent. Na_2SO_4	Per Cent. $NaOH$	$F_2O_3Al_2O_3$ SiO_2	$CaCO_3$ $MgCO_3$	H_2O
48	60.64	28.34	4.35	1.29	1.12	Traces	4.26
58	98.72	.54	.20		.10	.17	.26

52. Grading of Caustic Soda.—Caustic soda occurs on the market in a variety of grades and is sold on the basis of 60 per cent. of Na_2O. Caustic soda as a product of the alkali industry did not appear until 30 years after the industry was established in Great Britain, and the expression of its quality in the same terms as that of soda ash might therefore be expected. The molecular weight of caustic soda is 40; to arrive at sodium oxide, Na_2O, as an expression of the customary unit, 2 molecules, with a total molecular weight of 80, are used. In $2NaOH$ there are 63 parts, or 77.5 per cent. of Na_2O, the remainder being H_2O Therefore, a chemically pure caustic soda contains 77.5 per cent. of Na_2O, or its equivalent, 100 per cent. of $NaOH$. Following is given for comparison the percentage of the essential ingredient corresponding to, but never present in, the various grades of caustic commonly found in the market:

Grade	Per Cent. $NaOH$
60	77.42
70	90.32
72	92.90
74	95.48
76	98.06
77	99.35
77.5	100.00

Sodium chloride, sodium carbonate, and sodium sulphate, in varying proportions, constitute chiefly the remainder of the ingredients. With the present system of grading based on the chemical determination of the total alkali, the Na_2O content of the Na_2CO_3 is estimated with the Na_2O in terms of which the caustic soda, or $NaOH$, is expressed. With this method of expressing the quality of the caustic soda, the soap maker has just cause for complaint in that a variable percentage of an ingredient (sodium corbonate) not so valuable as the caustic soda is included in the total percentage of the essential ingredient present. The following is an industrial analysis of a sample of commercial caustic purporting to be of 74-per-cent. quality:

	Per Cent.
Total alkali, Na_2O	74.18
Total alkali, present as $NaOH$	69.88
Caustic alkali, $NaOH$	90.18
Combined alkali, Na_2CO_3	7.35
Sodium chloride, $NaCl$	2.02

This analysis indicates the sample to be of substantially 70-per-cent. quality. The difference between the sodium hydroxide actually present and that claimed, namely, 4.30 per cent. Na_2O, is due to the 7.35 per cent. of Na_2CO_3, this being estimated as its equivalent, 4.30 per cent. of Na_2O, in the total sodium oxide. As more or less carbonate is invariably present in all commercial caustic, especially in the lower grades, the system of including it in the expression of the quality of this product is open to severe criticism. Quotations of quality are thus confessedly a misrepresentation. The only rational method is the expression of the Na_2O as free caustic, or preferably units of $NaOH$.

This would be an absolute index of the value of the caustic as a saponifying agent, and not, as by the method in vogue, an uncertain approximation of the same. English degrees indicate the strength of the ash or the caustic in terms of Na_2O, but owing to an error in atomic weights, English analyses indicate a greater percentage of Na_2O than is present. This error has become so firmly established by tradition that modern ideas have been unable as yet to eliminate it. In Germany and Russia the strength is expressed in terms of sodium carbonate. This system is perfectly rational when applied to soda ash, but is inconsistent when applied to caustic. The expression of the value of commercial caustic soda in terms of an impurity is certainly not conducive to clear ideas on the subject, even though, in so far as the soap industry is concerned, this impurity is positively worthless as a saponifying agent for neutral glycerides.

53. The superior advantages and the economy of high-grade caustic need no argument. It is true of this product that the best, within certain limits, is the cheapest. The

variation in price arises from the slight differences in cost of production of the lower grades, combined, for those grades, with the proportionally greater cost of packages, transportation, etc.

The total charges contingent on marketing a 60-per-cent. caustic are the same as those of a 70-per-cent., although the former contains considerably less of the essential ingredient; also, the cost of production of a 70-per-cent. caustic is but little more than that of a 60-per-cent. The increased cost of production of the higher grades, namely, 74 per cent. and 76 per cent., makes necessary a higher price, which is less than it would be if cost of marketing were correspondingly increased.

54. Preparation of Caustic-Soda Lye.—The solid caustic soda is delivered at the works in the familiar sheet-iron drums, containing usually about 675 pounds. The dissolving of the solid caustic is a simple operation. The method employed in effecting solution, the arrangement of the tanks, and the system of transferring the lye, vary with each establishment.

The work of solution is facilitated by inserting a false bottom or cage in the bottom of the solution tank. The usual practice is to make a strong lye of 36°–40° Baumé, and dilute as needed. To make this strong lye the proper amount of water is run into the tank. The caustic soda in drums is rolled up to the tank, the plates on the heads are cut off and about twenty slashes with an axe made into the drum along its length. The drums are then lowered to the cage. The main draw-off cock is placed about 4 inches above the bottom of the tank so that the mud is not drawn when the lye is used. By making the solution in the afternoon it will be ready for use in the morning. At that time, the drums are taken out, examined for undissolved caustic, washed, and broken up for sale as scrap.

With this arrangement, a natural circulation of liquor of different densities is set up, with the result that weak liquor continually rises to the surface, while the saturated liquor,

by virtue of its greater density, goes to the bottom. This eliminates the mechanical agitation that is necessary when the solid caustic is allowed to rest on the bottom of the tank.

TABLE IV

PERCENTAGE OF SODIUM HYDRATE, *NaOH*, IN LYES OF DIFFERENT DENSITIES, MADE FROM CAUSTIC OF VARIOUS GRADES

Specific Gravity	Degrees Baumé	77½% %*NaOH*	76% %*NaOH*	74% %*NaOH*
1.075	10	6.55	6.42	6.25
1.091	12	8.00	7.84	7.63
1.116	15	10.06	9.86	9.60
1.142	18	12.64	12.40	12.07
1.162	20	14.37	14.09	13.72
1.180	22	15.91	15.61	15.19
1.210	25	18.58	18.23	17.74
1.241	28	21.42	20.99	20.44
1.263	30	23.67	23.21	22.60
1.320	35	28.83	28.28	27.53
Specific Gravity	**Degrees Baumé**	**72% %*NaOH***	**70% %*NaOH***	**60% %*NaOH***
1.075	10	6.08	5.91	5.06
1.091	12	7.43	7.22	6.19
1.116	15	9.34	9.08	7.78
1.142	18	11.74	11.41	9.78
1.162	20	13.35	12.97	11.12
1.180	22	14.78	14.36	12.31
1 210	25	17.27	16.78	14.38
1.241	28	19.89	19.33	16.57
1.263	30	21.99	21.37	18.32
1.320	35	26.79	26.04	22.31

55. In the preparation of caustic lyes of different densities from various grades of caustic, the effect of the

TABLE V

SPECIFIC GRAVITY OF CAUSTIC-SODA SOLUTIONS AT 15° C. (LUNGE)

Specific Gravity	Degrees Baumé	Degrees Twaddell	Per Cent. Na_2O	Per Cent. $NaOH$	1 Cubic Meter Contains Kilograms	
					Na_2O	$NaOH$
1.007	1	1.4	0.47	0.61	4	6
1.014	2	2.8	0.93	1.20	9	12
1.022	3	4.4	1.55	2.00	16	21
1.029	4	5.8	2.10	2.71	22	28
1.036	5	7.2	2.60	3.35	27	35
1.045	6	9.0	3.10	4.00	32	42
1.052	7	10.4	3.60	4.64	38	49
1.060	8	12.0	4.10	5.29	43	56
1.067	9	13.4	4.55	5.87	49	63
1.075	10	15.0	5.08	6.55	55	70
1.083	11	16.6	5.67	7.31	61	79
1.091	12	18.2	6.20	8.00	68	87
1.100	13	20.0	6.73	8.68	74	95
1.108	14	21.6	7.30	9.42	81	104
1.116	15	23.2	7.80	10.06	87	112
1.125	16	25.0	8.50	10.97	96	123
1.134	17	26.8	9.18	11.84	104	134
1.142	18	28.4	9.80	12.64	112	144
1.152	19	30.4	10.50	13.55	121	156
1.162	20	32.4	11.14	14.37	129	167
1.171	21	34.2	11.73	15.13	137	177
1.180	22	36.0	12.33	15.91	146	188
1.190	23	38.0	13.00	16.77	155	200
1.200	24	40.0	13.70	17.67	164	212
1.210	25	42.0	14.40	18.58	174	225
1.220	26	44.0	15.18	19.58	185	239
1.231	27	46.2	15.96	20.59	196	253
1.241	28	48.2	16.76	21.42	208	266
1.252	29	50.4	17.55	22.64	220	283
1.263	30	52.6	18.35	23.67	232	299
1.274	31	54.8	19.23	24.81	245	316
1.285	32	57.0	20.00	25.80	257	332
1.297	33	59.4	20.80	26.83	270	348
1.308	34	61.6	21.55	27.80	282	364
1.320	35	64.0	22.35	28.83	295	381
1.332	36	66.4	23.20	29.93	309	399
1.345	37	69.0	24.20	31.22	326	420
1.357	38	71.4	25.17	32.47	342	441
1.370	39	74.0	26.12	33.69	359	462
1.383	40	76.6	27.10	34.96	375	483
1.397	41	79.4	28.10	36.25	392	506
1.410	42	82.0	29.05	37.47	410	528
1.424	43	84.8	30.08	38.80	428	553
1.438	44	87.6	31.00	39.99	446	575
1.453	45	90.6	32.10	41.41	466	602
1.468	46	93.6	33.20	42.83	487	629
1.483	47	96.6	34.40	44.38	510	658
1.498	48	99.6	35.70	46.15	535	691
1.514	49	102.8	36.90	47.60	559	721
1.530	50	106.0	38.00	49.02	581	750

impurities, chiefly sodium chloride, sodium carbonate, and sodium sulphate, is to reduce the active value of the solution for the specific gravity indicated. This reduction in saponifying power is least for the highest grades and greatest for the lowest, as a natural result of the increased percentage of these impurities present. There is arranged in Table IV the percentage of sodium hydrate present in lyes of different densities, made from the usual grades of caustics, corresponding to the densities of lye made from chemically pure caustic. It is assumed that the total alkali which never actually occurs, is present entirely as caustic. The figures stated, for reasons previously given, are slightly higher than would be found in practice. However, this table possesses some value as a basis of comparison, and for many technical purposes the figures are suficiently accurate.

In the preparation of caustic-soda lye in the kettle room, the number of drums of caustic soda and the quantity of water required to furnish a lye of a certain density will be learned by experience. In Table V are given the densities of caustic-soda solutions made from chemically pure caustic soda.

56. Use of Caustic-Soda Lye.—The caustic-soda lye tank is usually situated in the kettle or soap-boiling room with an elevation of 3 or 4 feet above the tops of the kettles. It is placed at one end and piped to reach each kettle. The piping is arranged with stop valves so as not to interfere with any other boiling. Below the discharge cock, a water line is connected directly into the lye line running to the kettles. This makes it possible to deliver lye of any strength by controlling the lye and water valves. The soap boiler is provided with a Baumé hydrometer and draws the lye for test at the kettle into a cylinder or hydrometer jar as it is being delivered. A very good form of jar can be made from short pieces of pipe and fittings as shown in Fig. 6, wherein *a* may be regarded as a handle. When taking a sample the jar proper, *b*, is completely filled to *c* and the hydrometer dropped in, and the reading taken. By this means the lye is kept at the strength desired and is at all times under complete control.

57. Caustic Potash.—Potash, or crude potassium carbonate, was originally obtained from the ashes of seaweeds, and before the development of the Le Blanc process it provided the only saponifying agent then available. Later, wood ashes, beet-sugar residues, and wool scourings formed the chief commercial source. The various potassium salts are now obtained chiefly from the mineral carnallite, which is composed of the chlorides of potassium and magnesium with water of crystallization. Carnallite, with other minerals composed of chlorides and sulphates of the alkali and alkaline earth metals, occurs in immense deposits near Stassfurt, Germany.

Fig. 6

Caustic potash is manufactured from carnallite by the Le Blanc process. The potassium chloride is converted into potassium sulphate by treatment with sulphuric acid. A mixture is then obtained that is analogous to the crude Glauber's salt of the Le Blanc process. This mixture is fused with limestone and coal, and the resulting mass lixiviated with water. The solution of potassium carbonate thus obtained is causticized with lime, and a solution of caustic potash results. This caustic liquor is removed, evaporated to dryness, and fused. While molten it is run into drums and comes into commerce as caustic potash. It is not so uniform in its composition as the corresponding sodium compound. Commercial caustic potash is a mixture of the following substances:

	Per Cent.
Carbonate and hydrate of potassium	80 to 95
Chlorides of sodium and potassium	5 to 10
Sulphate of potassium	5 to 15
Insoluble matter	1.5 to 3

A good caustic potash is generally opaque and of a dull-gray slate or bluish color, often streaked with red or greenish stains. It has a powerful affinity for moisture, and on expo-

TABLE VI

SPECIFIC GRAVITY OF SOLUTIONS OF CAUSTIC POTASH AT 15° C. (LUNGE)

Specific Gravity	Degrees Baumé	Degrees Twaddell	Per Cent. K_2O	Per Cent. KOH	1 Cubic Meter Contains Kilograms	
					K_2O	KOH
1.007	1	1.4	.7	.9	7	9
1.014	2	2.8	1.4	1.7	14	17
1.022	3	4.4	2.2	2.6	22	26
1.029	4	5.8	2.9	3.5	30	36
1.037	5	7.4	3.8	4.5	39	46
1.045	6	9.0	4.7	5.6	49	58
1.052	7	10.4	5.4	6.4	57	67
1.060	8	12.0	6.2	7.4	66	78
1.067	9	13.4	6.9	8.2	74	88
1.075	10	15.0	7.7	9.2	83	99
1.083	11	16.6	8.5	10.1	92	109
1.091	12	18.2	9.2	10.9	100	119
1.100	13	20.0	10.1	12.0	111	132
1.108	14	21.6	10.8	12.9	119	143
1.116	15	23.2	11.6	13.8	129	153
1.125	16	25.0	12.4	14.8	140	167
1.134	17	26.8	13.2	15.7	150	178
1.142	18	28.4	13.9	16.5	159	188
1.152	19	30.4	14.8	17.6	170	203
1.162	20	32.4	15.6	18.6	181	216
1.171	21	34.2	16.4	19.5	192	228
1.180	22	36.0	17.2	20.5	203	242
1.190	23	38.0	18.0	21.4	214	255
1.200	24	40.0	18.8	22.4	226	269
1.210	25	42.0	19.6	23.3	237	282
1.220	26	44.0	20.3	24.2	248	295
1.231	27	46.2	21.1	25.1	260	309
1.241	28	48.2	21.9	26.1	272	324
1.252	29	50.4	22.7	27.0	284	338
1.263	30	52.6	23.5	28.0	297	353
1.274	31	54.8	24.2	28.9	308	368
1.285	32	57.0	25.0	29.8	321	385
1.297	33	59.4	25.8	30.7	335	398
1.308	34	61.6	26.7	31.8	349	416
1.320	35	64.0	27.5	32.7	363	432
1.332	36	66.4	28.3	33.7	377	449
1.345	37	69.0	29.3	34.9	394	469
1.357	38	71.4	30.2	35.9	410	487
1.370	39	74.0	31.0	36.9	425	506
1.383	40	76.6	31.8	37.8	440	522
1.397	41	79.4	32.7	38.9	457	543
1.410	42	82.0	33.5	39.9	472	563
1.424	43	84.8	34.4	40.9	490	582
1.438	44	87.6	35.4	42.1	509	605
1.453	45	90.6	36.5	43.4	530	631
1.468	46	93.6	37.5	44.6	549	655
1.483	47	96.6	38.5	45.8	571	679
1.498	48	99.6	39.6	47.1	593	706
1.514	49	102.8	40.6	48.3	615	731
1.530	50	106.0	41.5	49.4	635	756
1.546	51	109.2	42.5	50.6	655	779
1.563	52	112.6	43.6	51.9	681	811
1.580	53	116.0	44.7	53.2	706	840
1.597	54	119.4	45.8	54.5	731	870
1.615	55	123.0	47.0	55.9	754	902
1.634	56	126.8	48.3	57.5	789	940

sure to the air, it deliquesces rapidly and soon becomes pasty. Sometimes, it presents a whitish appearance in the center of the drum, and occasionally it is honeycombed. That which contains a large porportion of salts is usually crystaline and very compact. Its high cost militates against its more general use as a saponifying agent; and it is used very little today in soap manufacture. On exposure to the air, its solutions rapidly absorb carbon dioxide, with the formation of the acid carbonate. As a chemical agent it is more active than caustic soda. Caustic potash improves the quality of all soaps of which it is an ingredient. It cannot be used in settled soap manufacture with sodium chloride as the graining agent, because an interchange of alkalies would take place and much of the potassium would be lost as the chloride. Soaps containing it are milder in their detersive action, will stand more filling without efflorescence, and possess a tougher texture.

By virtue of their milder detersive action on animal and vegetable fibers, potash soaps—usually soft soaps—find wide application in the textile industry.

In Table VI is given the specific gravity of solutions of caustic potash at 15° C., according to Lunge.

MEASUREMENT OF THE DENSITY OF LIQUIDS

58. The **specific gravity** of a liquid or solid is the expression of the relation between the weight of the liquid or solid and the weight of an equal volume of pure water at a definite temperature, usually 15° C. The most convenient and practical means of ascertaining the strength of solutions of carbonated and caustic alkalies is to determine their specific gravity with a hydrometer. As shown in Fig. 7, the hydrometer is simply a closed tube with a bulb blown in one end, containing a paper scale and filled with shot or murcury. When placed in a liquid, the weighted bulb enables the hydrometer to float in an upright position. The Baumé and Twaddell hydrometers are the instruments most commonly used, the Baumé

Fig. 7

hydrometer in America and the Twaddell hydrometer in England.

With the latter instrument, the density of pure distilled water is represented by zero, and the scale is graduated in such a manner that the specific gravity of the liquid may be cal-

TABLE VII

SPECIFIC GRAVITY AND DEGREES BAUMÉ (AMERICAN STANDARD) FOR LIQUIDS HEAVIER THAN WATER AT 60° F. (OLSEN)

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
0	1.0000	24	1.1983	48	1.4948
1	1.0069	25	1.2083	49	1.5104
2	1.0140	26	1.2185	50	1.5263
3	1.0211	27	1.2288	51	1.5426
4	1.0284	28	1.2393	52	1.5591
5	1.0357	29	1.2500	53	1.5761
6	1.0432	30	1.2609	54	1.5934
7	1.0507	31	1.2719	55	1.6111
8	1.0584	32	1.2832	56	1.6292
9	1.0662	33	1.2946	57	1.6477
10	1.0741	34	1.3063	58	1.6667
11	1.0821	35	1.3182	59	1.6860
12	1.0902	36	1.3303	60	1.7059
13	1.0985	37	1.3426	61	1.7262
14	1.1069	38	1.3551	62	1.7470
15	1.1154	39	1.3679	63	1.7683
16	1.1240	40	1.3810	64	1.7901
17	1.1328	41	1.3942	65	1.8125
18	1.1417	42	1.4078	66	1.8354
19	1.1508	43	1.4216	67	1.8590
20	1.1600	44	1.4356	68	1.8831
21	1.1694	45	1.4500	69	1.9079
22	1.1789	46	1.4646	70	1.9333
23	1.1885	47	1.4796		

culated by multiplying the number of degrees registered on the scale by .005 and adding the product to 1; thus, the density of a liquid indicating 100° Twaddell would be $100 \times .005 + 1.000$, or 1.500. The Twaddell hydrometer is a direct-reading instrument. This means that the reading on the

scale shows the specific gravity of the liquid directly as compared with pure water at the definite temperature.

The Baumé hydrometer is adapted for the determination of the specific gravity of liquids, either heavier or lighter than water (see Tables VII and VIII). The scale used is arbitrary

TABLE VIII

SPECIFIC GRAVITY AND DEGREES BAUMÉ FOR LIQUIDS LIGHTER THAN WATER AT 60° F. (OLSEN)

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
10	1.0000	34	.8537	58	.7447
11	.9929	35	.8485	59	.7407
12	.9859	36	.8434	60	.7368
13	.9790	37	.8383	61	.7330
14	.9722	38	.8333	62	.7292
15	.9655	39	.8284	63	.7254
16	.9589	40	.8235	64	.7216
17	.9524	41	.8187	65	.7179
18	.9459	42	.8140	66	.7143
19	.9396	43	.8092	67	.7107
20	.9333	44	.8046	68	.7071
21	.9272	45	.8000	69	.7035
22	.9211	46	.7955	70	.7000
23	.9150	47	.7910	71	.6965
24	.9091	48	.7865	72	6931
25	.9032	49	.7821	73	.6897
26	.8974	50	.7778	74	.6863
27	.8917	51	.7735	75	.6829
28	.8861	52	.7692	76	.6796
29	.8805	53	.7650	77	.6763
30	.8750	54	.7609	78	.6731
31	.8696	55	.7568	79	.6699
32	.8642	56	.7527	80	.6667
33	.8589	57	.7487		

and bears no direct relation to the specific gravity; hence, the conversion of the readings into the corresponding specific gravity is done by reference to tables prepared for this purpose. In Table IX are given the values of specific gravity corresponding to degrees Twaddell and degrees Baumé.

TABLE IX

SPECIFIC GRAVITY, DEGREES TWADDELL, AND DEGREES BAUMÉ

Twaddell	Degrees Baumé	Specific Gravity	Degrees Twaddell	Degrees Baumé	Specific Gravity	Degrees Twaddell	Degrees Baumé	Specific Gravity	Degrees Twaddell	Degrees Baumé	Specific Gravity
0	.0	1.000	44	26.2	1.220	88	44.3	1.440	132	57.7	1.660
1	.7	1.005	45	26.6	1.225	89	44.7	1.445	133	57.9	1.665
2	1.4	1.010	46	27.1	1.230	90	45.0	1.450	134	58.2	1.670
3	2.1	1.015	47	27.6	1.235	91	45.3	1.455	135	58.4	1.675
4	2.8	1.020	48	28.1	1.240	92	45.7	1.460	136	58.7	1.680
5	3.5	1.025	49	28.5	1.245	93	46.0	1.465	137	58.9	1.685
6	4.2	1.030	50	29.0	1.250	94	46.4	1.470	138	59.2	1.690
7	4.9	1.035	51	29.5	1.255	95	46.7	1.475	139	59.5	1.695
8	5.6	1.040	52	29.9	1.260	96	47.0	1.480	140	59.7	1.700
9	6.2	1.045	53	30.4	1.265	97	47.4	1.485	141	60.0	1.705
10	6.9	1.050	54	30.8	1.270	98	47.7	1.490	142	60.2	1.710
11	7.6	1.055	55	31.3	1.275	99	48.0	1.495	143	60.5	1.715
12	8.2	1.060	56	31.7	1.280	100	48.4	1.500	144	60.7	1.720
13	8.8	1.065	57	32.2	1.285	101	48.7	1.505	145	60.9	1.725
14	9.5	1.070	58	32.6	1.290	102	49.0	1.510	146	61.2	1.730
15	10.1	1.075	59	33.0	1.295	103	49.3	1.515	147	61.4	1.735
16	10.7	1.080	60	33.5	1.300	104	49.6	1.520	148	61.7	1.740
17	11.4	1.085	61	33.9	1.305	105	49.9	1.525	149	61.9	1.745
18	12.0	1.090	62	34.3	1.310	106	50.2	1.530	150	62.4	1.750
19	12.6	1.095	63	34.7	1.315	107	50.6	1.535	151	62.6	1.755
20	13.2	1.100	64	35.1	1.320	108	50.8	1.540	152	62.8	1.760
21	13.8	1.105	65	35.6	1.325	109	51.2	1.545	153	63.1	1.765
22	14.4	1.110	66	36.0	1.330	110	51.5	1.550	154	63.3	1.770
23	15.0	1.115	67	36.4	1.335	111	51.8	1.555	155	63.5	1.775
24	15.5	1.120	68	36.8	1.340	112	52.1	1.560	156	63.8	1.780
25	16.1	1.125	69	37.2	1.345	113	52.3	1.565	157	64.0	1.785
26	16.7	1.130	70	37.6	1.350	114	52.6	1.570	158	64.2	1.790
27	17.2	1.135	71	38.0	1.355	115	52.9	1.575	159	64.4	1.795
28	17.8	1.140	72	38.4	1.360	116	53.2	1.580	160	64.7	1.800
29	18.4	1.145	73	38.8	1.365	117	53.5	1.585	161	64.9	1.805
30	18.9	1.150	74	39.2	1.370	118	53.8	1.590	162	65.1	1.810
31	19.5	1.155	75	39.5	1.375	119	54.1	1.595	163	65.2	1.815
32	20.0	1.160	76	39.9	1.380	120	54.3	1.600	164	65.3	1.820
33	20.5	1.165	77	40.3	1.385	121	54.7	1.605	165	65.5	1.825
34	21.1	1.170	78	40.7	1.390	122	54.9	1.610	166	65.7	1.830
35	21.6	1.175	79	41.1	1.395	123	55.2	1.615	167	66.0	1.835
36	22.1	1.180	80	41.5	1.400	124	55.5	1.620	168	66.2	1.840
37	22.6	1.185	81	41.8	1.405	125	55.8	1.625	169	66.4	1.845
38	23.2	1.190	82	42.2	1.410	126	56.0	1.630	170	66.7	1.850
39	23.7	1.195	83	42.5	1.415	127	56.3	1.635	171	66.9	1.855
40	24.2	1.200	84	42.9	1.420	128	56.6	1.640	172	67.0	1.860
41	24.7	1.205	85	43.2	1.425	129	56.9	1.645	173	67.5	1.865
42	25.2	1.210	86	43.6	1.430	130	57.1	1.650			
43	25.7	1.215	87	44.0	1.435	131	57.4	1.655			

CHEMISTRY OF SOAP MANUFACTURE

59. In the preceding examination of the raw materials of soap manufacture there have been considered those bodies which carry the two compounds—namely, a glyceride and a caustic alkali—that, when in chemical combination, form soap. Soap boiling, therefore, consists essentially in bringing a fatty body and a caustic alkali in aqueous solution in contact under suitable conditions, whereby a simple chemical reaction takes place with the formation of an alkaline salt of a fatty acid and the liberation of glycerine. This reaction is known as *saponification.*

60. For the purpose of explanation, the fatty body will be represented by 1 molecule of stearin and the saponifying agent by 3 molecules of caustic soda; thus:

$$\underset{\text{stearin}}{C_3H_5(C_{18}H_{35},O_2)_3}+\underset{\text{caustic soda}}{3NaOH}=\underset{\text{glycerine}}{C_3H_5(OH)_3}+\underset{\text{sodium stearate}}{3C_{18}H_{35}O_2Na}$$

The term saponification is also applicable to a vast number of similar chemical changes in which an alcohol is set free and an acid is produced, when water is the saponifying agent, or an alkaline salt of the fatty acid, that is, soap, when the saponifying agent is an alkali.

GLYCERIDES AND THEIR PROPERTIES

61. In order to understand thoroughly the soap-making properties of the various fats and oils and their behavior in the soap kettle, it is necessary to be familiar with the chemical properties of the various glycerides that constitute the fats and oils employed in soap manufacture. The variation in the amount of alkali absorbed by any particular fat or oil arises from differences in the composition of the glycerides themselves and from the varying proportions in which the glycerides occur in any particular stock. It is a well known fact that fats and oils are indefinite mixtures of various glycerides, and that the amount of alkali absorbed is influenced by the nature of the glycerides characteristic of the stock.

TA

ACIDS OF THE ACETIC SERI

Acid	Formula	Mol. Wt.	Corresponding Glyceride	Formula	Mol. Wt.	Per C Na A so
Formic	$H \cdot COOH$	46	Formin	$C_3H_5(O \cdot HCO)_3$	176	68
Acetic	$CH_3 \cdot COOH$	60	Acetin	$C_3H_5(O \cdot CH_3CO)_3$	218	55
Propionic	$C_2H_5 \cdot COOH$	74	Propionin	$C_3H_5(O \cdot C_2H_5CO)_3$	260	46
Butyric	$C_3H_7 \cdot COOH$	88	Butyrin	$C_3H_5(O \cdot C_3H_7CO)_3$	302	39
Valeric	$C_4H_9 \cdot COOH$	102	Valerin	$C_3H_5(O \cdot C_4H_9CO)_3$	344	34
Caproic	$C_5H_{11} \cdot COOH$	116	Caproin	$C_3H_5(O \cdot C_5H_{11}CO)_3$	386	31
Oenanthylic	$C_6H_{13} \cdot COOH$	130	Oenanthylin	$C_3H_5(O \cdot C_6H_{13}CO)_3$	428	28
Caprylic	$C_7H_{15} \cdot COOH$	144	Caprylin	$C_3H_5(O \cdot C_7H_{15}CO)_3$	470	25
Pelargonic	$C_8H_{17} \cdot COOH$	158	Pelargonin	$C_3H_5(O \cdot C_8H_{17}CO)_3$	512	23
Capric	$C_9H_{19} \cdot COOH$	172	Caprin	$C_3H_5(O \cdot C_9H_{19}CO)_3$	554	21
Undecylic	$C_{10}H_{21} \cdot COOH$	186	Undecylin	$C_3H_5(O \cdot C_{10}H_{21}CO)_3$	596	2
Lauric	$C_{11}H_{23} \cdot COOH$	200	Laurin	$C_3H_5(O \cdot C_{11}H_{23}CO)_3$	638	1
Tridecylic	$C_{12}H_{25} \cdot COOH$	214	Tridecylin	$C_3H_5(O \cdot C_{12}H_{25}CO)_3$	680	1
Myristic	$C_{13}H_{27} \cdot COOH$	228	Myristin	$C_3H_5(O \cdot C_{13}H_{27}CO)_3$	722	1
Pentadecatoic	$C_{14}H_{29} \cdot COOH$	242	Pentadecatorin	$C_3H_5(O \cdot C_{14}H_{29}CO)_3$	764	1
Palmitic	$C_{15}H_{31} \cdot COOH$	256	Palmitin	$C_3H_5(O \cdot C_{15}H_{31}CO)_3$	806	1
Margaric	$C_{16}H_{33} \cdot COOH$	270	Margarin	$C_3H_5(O \cdot C_{16}H_{33}CO)_3$	848	1
Stearic	$C_{17}H_{35} \cdot COOH$	284	Stearin	$C_3H_5(O \cdot C_{17}H_{35}CO)_3$	890	1
Nondecylic	$C_{18}H_{37} \cdot COOH$	298	Nondecylin	$C_3H_5(O \cdot C_{18}H_{37}CO)_3$	932	1
Arachidic	$C_{19}H_{39} \cdot COOH$	312	Arachidin	$C_3H_5(O \cdot C_{19}H_{39}CO)_3$	974	1
Medullic	$C_{20}H_{41} \cdot COOH$	326	Medullin	$C_3H_5(O \cdot C_{20}H_{41}CO)_2$	1,016	1
Behenic	$C_{21}H_{43} \cdot COOH$	340	Behenin	$C_3H_5(O \cdot C_{21}H_{43}CO)_3$	1,058	1
Carnaübic	$C_{23}H_{47} \cdot COOH$	368	Carnaübin	$C_3H_5(O \cdot C_{23}H_{47}CO)_3$	1,142	1
Hyenic	$C_{24}H_{49} \cdot COOH$	382	Hyenin	$C_3H_5(O \cdot C_{24}H_{49}CO)_3$	1,184	1
Cerotic	$C_{26}H_{53} \cdot COOH$	410	Cerotin	$C_3H_5(O \cdot C_{26}H_{53}CO)_3$	1,268	
Melissic	$C_{29}H_{59} \cdot COOH$	452	Melissin	$C_3H_5(O \cdot C_{29}H_{59}CO)_3$	1,394	

ACIDS OF THE ACRYLIC SERI

Acrylic	$C_2H_3 \cdot COOH$	72		$C_3H_5(O \cdot C_2H_3CO)_3$	254	
Crotonic	$C_3H_5 \cdot COOH$	86		$C_3H_5(O \cdot C_3H_5CO)_3$	296	
Angelic, Tiglic	$C_4H_7 \cdot COOH$	100		$C_3H_5(O \cdot C_4H_7CO)_3$	338	3
Hypogaric	$C_{15}H_{29} \cdot COOH$	254		$C_3H_5(O \cdot C_{15}H_{29}CO)_3$	800	1
Oleic	$C_{17}H_{33} \cdot COOH$	282	Olein	$C_3H_5(O \cdot C_{17}H_{33}CO)_3$	884	1

ACIDS OF THE LINOLIC SERIE

Elæomargaric	$C_{16}H_{29} \cdot COOH$	266	Elæomargarin	$C_3H_5(O \cdot C_{16}H_{29}CO)_3$	836	1
Linolic	$C_{17}H_{31} \cdot COOH$	280	Linolein	$C_3H_5(O \cdot C_{17}H_{31}CO)_3$	878	1

ACIDS OF THE LINOLENIC SER

Linolenic	$C_{17}H_{29} \cdot COOH$	278	Linolenin	$C_3H_5(O \cdot C_{17}H_{29}CO)_3$	872	1

ACIDS OF THE RECINOLEIC S

Recinoleic	$C_{17}H_{32}OH \cdot COOH$	298	Recinolein	$C_3H_5(O \cdot C_{17}H_{32} \cdot OH \cdot CO)_3$	932	1

GENERAL FORMULA, $C_nH_{2n+1}COOH$

Per Cent. of Glycerine Set Free	Per Cent. of Fatty Acids Set Free	Natural Source
52.28	78.41	The acid occurs in bodies of ants, in the stinging pine, and in certain nettles.
42.20	82.56	Occurs naturally only in slight quantities in oil of *Euonymus Europæus.*
35.38	85.38	Occurs in small quantities in the fruit of Gingko biloba.
30.47	87.42	Cow's butter.
26.74	88.94	The acid occurs in the animal and vegetable kingdoms, free, and as an ester.
23.83	90.16	Cow's butter, coconut, and palm-kernel oils.
21.50	91.14	Occurs in small quantities in Kalmus oil.
19.57	91.91	Cow's butter, coconut, and palm-kernel oils.
17.97	92.58	The acid occurs naturally in leaves of *Pelargonium roseum.*
16.61	93.13	Cow's butter, coconut, and palm-kernel oils.
15.44	93.63	
14.42	94.06	Spermaceti, tan oil, coconut, and palm-kernel oils.
13.53	94.41	
12.75	94.75	Spermacetic, muscat butter, coconut, and palm-kernel oils.
12.04	95.03	
11.41	95.30	Associated with stearin and olein in most animal and vegetable fats and oils.
10.85	95.52	Seeds of thorn apple, *Datura Stramonium.*
10.34	95.72	See palmitin.
9.87	95.92	
9.44	96.10	Characteristic glyceride of peanut oil.
9.06	96.27	Medullic acid is a mixture of palmitic and stearic acids.
8.69	96.40	Characteristic glyceride of oil of *ben.*
8.05	96.65	Occurs as an ether in combination with the higher alcohols in carnaübic wax
7.77	96.79	Free acid occurs in glandular pouches of the striped hyena.
7.25	96.99	Acid occurs in free state in beeswax and carnaübic waxes.
6.60	97.25	Acid occurs in free state in beeswax.

ENERAL FORMULA, $C_nH_{2n-1}COOH$

		The acid is an oxidation product of acrolein.
		Acid occurs with isocrotonic acid in crude pyroligneous acid.
27.22	88.76	Angelic acid occurs in angelica root. Glyceride occurs in croton oil.
11.49	95.26	Present in peanut oil.
10.41	95.70	The characteristic glyceride of all liquid fats.

NERAL FORMULA, $C_nH_{2n-3}COOH$

11.01	95.69	Occurs in Japanese wood oil.
10.48	95.68	Occurs in linseed and other drying oils.

ENERAL FORMULA, $C_nH_{2n-5}COOH$

10.55	95.64	Occurs in drying oils, especially linseed oil.

-GENERAL FORMULA, $C_nH_{2n-2}O_3$

9.87	95.92	Characteristic glyceride of castor oil.

It will be seen from Table X that the amount of alkali required for saturation decreases as the molecular weight of the glycerides increases. Hence, it will be found that those commercial fats and oils in which the glycerides of low molecular weight occur, possess the highest alkali absorption in proportion to their weight.

The greater quantity of salt required for graining the soap made from such stock is due to the presence of those glycerides of low molecular weight whose greater solubility in brine of the sodium salt is a marked characteristic. As the glycerides increase in molecular weight, the solubility in brine of the soap obtained therefrom diminishes; hence, less salt is required for graining.

NOTE.—As shown in *Organic Chemistry*, the homologous character of the simple hydrocarbons of the saturated and unsaturated fatty series extends to all compounds formed from them, either naturally or artificially. The purpose of Table X is to illustrate this property by extending the quantitative characteristics of the more important acids to their corresponding glycerides, and more particularly to those employed in soap manufacture, which appear in heavy type. This table is of great practical interest from the standpoint of both the candle maker and the soap boiler, inasmuch as the most important practical properties of glycerides, namely, alkali absorption and glycerine liberation, are set forth in detail. It will be seen from the standpoint of the soap maker that to the acetic and acrylic series of fatty bodies belong the most important commercial glycerides, namely, stearin, palmitin, and olein, while to the more unsaturated series belong those glycerides characteristic of all drying oils, which are the special consideration of the paint manufacturer.

62. The homologous properties of the glycerides mentioned in the previous article and shown in Table X, are further shown in their practical application in soap making in Table XI, in which is indicated the theoretical yield of anhydrous soap from the glycerides mentioned.

63 The reason for the greater yield of soap from coconut oil than from the ordinary animal and vegetable fats is thus made clear Not only is there a greater yield of anhydrous soap in itself, but by virtue of that higher yield a greater degree of hydration and *filling* is thus permissible. In Table XII are given the actual and not the theoretical percentages of caustic potash and caustic soda required in practice to saponify the commercial fats and oils mentioned.

TABLE XI

THEORETICAL YIELD OF ANHYDROUS SOAP

Glyceride and Chief Sources	Molecular Weight	Yield on Saponification With Water		Per Cent. Water Absorbed	Yield on Saponification With Caustic Soda		Per Cent. *NaOH* Absorbed
		Per Cent. Fatty Acids	Per Cent. Glycerine		Per Cent. Soap	Per Cent. Glycerine	
Laurin—coconut and palm-kernel oils	638	94.04	14.42	8.46	104.38	14.42	18.80
Myristin—palm-kernel oils	722	94.74	12.75	7.48	103.87	12.70	16.63
Palmitin—palm oil and tallow	806	95.28	11.41	6.69	103.47	11.41	14.88
Linolein—linseed oil	878	95.68	10.48	6.16	103.19	10.48	13.67
Olein—olive and cottonseed oils . . .	884	95.70	10.40	6.10	103.16	10.40	13.56
Stearin—tallow and lard	890	95.73	10.34	6.07	103.14	10.34	13.48
Recinolein—castor oil	932	95.92	9.88	5.80	103.00	9.88	12.88
Arachidin—peanut oil	974	96.10	9.44	5.54	102.87	9.44	12.31

TABLE XII

PERCENTAGES OF CAUSTIC POTASH AND CAUSTIC SODA TO SAPONIFY COMMERCIAL FATS AND OILS

	Per Cent. *KoH*	Per Cent. *NaOH*
Almond oil	19.5–19.6	13.9–14
Bone fat and grease	19.1–19.7	13.6–14
Butter	22.1–23.2	15.8–16.5
Castor Oil	17.6–18.1	12.5–13
Cod oil	18.5–21.3	13.2–15.1
Cottonseed oil	19.1–19.6	13.6–14
Coconut oil	24.6–26.8	17.5–19.1
Hempseed oil	19.3	13.8
Linseed oil	18.7–19.5	13.3–14
Lard oil	19.2–19.6	13.7–14
Niger seed oil	18.9–19.1	13.5–13.6
Olive oil	19.1–19.6	13.6–14
Peanut oil	19.1–19.6	13.6–14
Palm oil	19.6–20.2	14–14.4
Palm nut oil	22–24.7	15.7–17.7
Porpoise oil	21.6	15.5
Poppy seed oil	19.3–19.5	13.8–14
Rape oil	17.1–17.9	12.2–12.8
Rosin	17–19.3	12.1–14
Seal oil	18.9–19.6	13.5–14
Sesame oil	19–19.4	13.9–14
Sperm oil	12.3–14	8.8–10
Tallow	19.3–19.8	13.7–14.1
Walnut oil	19.6	14
Whale oil	18.8–22.4	13.4–16

BEHAVIOR OF FATS AND OILS TOWARD SAPONIFYING AGENTS

64. The various fats and oils display different characteristics in their behavior toward saponifying agents. Moreover, the chemical reactions of organic compounds do not proceed with the ease and certainty that characterize the reactions of inorganic compounds. In effecting combination between fats or oils and caustic alkalies in a soap kettle, where in many instances the fatty bodies are in excess of 100,000 pounds, the chemical peculiarities of the bodies undergoing change should in every case be thoroughly understood.

65. In a mixture of fats, the individual fats tend to impart their properties to one another. Certain oils, notably coconut and palm kernel, require caustic lye of high density to effect combination. With others, as tallow and palm oil, saponification takes place readily with caustic lye of lower density. Coconut oil requires a caustic lye of at least 20° Baumé, while tallow can be completely saponified with lye no stronger than 18° Baumé. When soap stocks with these characteristics are mixed, the requirements of each are modified so that an oil requiring for saponification alone a lye of high density enters into combination with lye of a density with which it would not combine otherwise without the consumption of a great deal of time and labor. On the other hand, that stock requiring naturally for ready saponification a lye of low density enters readily into combination with a lye of higher density. These peculiarities will be considered in due order.

66. Saponification of Tallow.—Tallow requires a caustic lye of comparatively low density for satisfactory saponification. A 12° Baumé lye, when no subsequent dilution is made, is considered to give the best results. On boiling with open steam, a lye of 18° to 20° Baumé is the highest density practicable. When open steam is used with caustic lye of this density, tallow is the most easily saponified of all glyceride soap stocks, and the soap formed is most easily grained.

Sodium stearate, which constitutes the bulk of the anhydrous soap made from tallow, is one of the least soluble in water of all the alkaline salts of the fatty acids, as it undergoes practically no change when treated with 10 parts of water; neither is its hardness appreciably affected. This quality manifests itself in the inferior lathering properties of pure tallow soap.

For this reason other oils are used. In making a laundry soap, rosin is added for the same purpose. Furthermore,

TABLE XIII

POUNDS OF TALLOW SAPONIFIED BY 100 POUNDS OF CAUSTIC SODA OF DIFFERENT DENSITIES MADE FROM VARIOUS GRADES OF CAUSTIC

Density, Degrees Baumé	Grade of Caustic Soda					
	77½ Per Cent. Na_2O	76 Per Cent. Na_2O	74 Per Cent. Na_2O	72 Per Cent. Na_2O	70 Per Cent. Na_2O	60 Per Cent. Na_2O
	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds	Tallow Saponified Pounds
10	46.78	45.86	44.66	43.45	42.24	36.20
12	57.14	56.03	54.55	53.08	51.59	48.49
15	71.85	70.46	68.60	66.74	64.88	60.96
18	90.02	88.26	85.94	83.62	81.28	69.66
20	102.64	100.60	97.95	95.30	92.64	79.39
22	113.64	111.40	108.50	105.50	102.60	87.92
25	132.71	130.10	126.70	123.30	119.90	102.70
28	153.00	150.10	146.10	142.10	138.10	118.40
30	169.07	165.80	161.40	157.00	152.60	130.80
35	205.92	201.90	196.60	191.30	186.00	159.30

on aging, a pure tallow soap becomes so hard as to give very little lather, so that its use is not economical for either household or laundry purposes. The comparative insolubility in water of sodium stearate is also shown in the readiness with which tallow soap dries. Its presence in admixture with other fats imparts firmness, or body, to the soap, thus enabling a greater proportion of softer stock, or that fatty acid whose sodium salt has a greater affinity for water, to be incorporated.

The use of sodium stearate thus increases the amount of water that may be incorporated with a soap without an excessive sacrifice of firmness. It is the best raw material for the manufacture of grained soaps and admits of the greatest yield of all the animal soap stocks. With its use, the various chemical and physical changes occurring in the soap kettle during the process of boiling are well defined and of easy recognition.

67. In Table XIII is expressed the saponifying power of caustic lyes of different densities made from chemically pure and ordinary grades of caustic occurring in the market. By this table, the amount of stock that can be saponified by any quantity of lye of the density and quality given may be readily determined within limits of accuracy suitable for all technical purposes to which the table may be applicable.

68. Saponification of Cottonseed Oil.—Refined cottonseed oil saponifies with difficulty and only after continued boiling, especially when saponified alone. The absence of free fatty acids tends to retard saponification. Combination with alkali is hastened when tallow is present, or upon the addition of soap scraps. Saponification is best begun with a 15° Baumé lye.

Pure cottonseed-oil soap is white, with a firmness determined largely by its degree of hydration. It consists almost entirely of sodium oleate. This compound is soluble in 10 parts of water, while sodium stearate, as already shown, is not appreciably affected by this volume. In accordance with its greater solubility in water, sodium oleate has in comparison greater and peculiar lathering properties. It lathers more readily than does sodium stearate, but instead of the firm lather of tallow soap, obtained only after much rubbing, it gives a shiny, thin lather peculiar to all soaps made of stock consisting largely of olein, for example, Castile soap and cottonseed-oil soap stock. Cottonseed oil is generally used in admixture with varying proportions of tallow and grease.

A good settled soap of cottonseed oil alone is not practicable. Soap thus made is *thin* and lacks the body and durability of

a tallow soap or a soap made from mixed stock. By the use, however, of a large proportion of soda ash and sodium silicate, an artificial firmness may be imparted.

Cottonseed-oil soaps *sweat* readily, and unless the oil has been refined with care, they discolor rapidly and become rancid. The brownish or yellowish blotches seen in soaps containing cottonseed oil may be traced to the imperfect removal of the coloring matter of the seed during the refining process.

69. Saponification of Coconut and Palm-Kernel Oils.—Coconut and palm-kernel oils differ from all fatty bodies employed in soap manufacture in the greater quantity of alkali required for saponification, in the greater quantity of salt required for graining, and in the greater yield of soap produced, the quality of which permits the greatest amount of hydration and filling. The difficulty of graining these soaps with dry salt or brine is overcome by using strong caustic lye for graining.

Pure coconut-oil soap is white, brittle, and hard. The oil is a valuable addition to cottonseed oil and tallow, and it yields a soap possessing qualities superior to that possessed by either stock alone. It enters into combination with alkali with extreme ease, which property especially adapts it for soap manufacture by the cold process.

During saponification considerable heat is evolved, and when once begun, saponification takes place with such rapidity that the contents of the kettle, unless carefully watched, will boil over. On the stock change (stock saponification), difficulty is often experience in working with coconut oil, or a mixture of oils containing coconut oil, the soap mass becoming thick easily. This is due to the high absorption of water consequent to rapid saponification and may be overcome by retarding the rate of combination of caustic alkali and oil. This is best effected by adding brine when the soap mass shows signs of becoming thick. It may also be provided by adding the oil slowly to the caustic alkali already in the kettle, at the same time boiling vigorously.

70. Coconut oil combines with weak and strong caustic lyes with equal facility, but in practice in the boiling of settled soap, a density of from 20° to 25° Baumé is commonly used. Coconut-oil soap when hot is very fluid, smooth, and transparent; when cold, it becomes so hard as to be cut only with difficulty. It dissolves readily in water, yielding a quickly formed, profuse, but not permanent, lather. It is caustic to the tongue even though no free alkali is present, and when used for toilet purposes in excess of actual requirements, it irritates and reddens the skin. If coconut oil is not completely saponified, the soap made from it soon becomes rancid and odorous. It dissolves freely in salt water and is the fatty basis of the so-called marine, or salt-water, soaps.

71. The complex composition of coconut oil suffices to explain the peculiarities of its behavior toward saponifying agents and the properties of the soap made from it. Coconut and palm-kernel oils contain a greater variety and quantity of glycerides of fatty acids of low molecular weight than any other soap stock.

As will be seen by referring to Table XI, these bodies possess a higher alkali absorption, yield a greater percentage of glycerine on saponification, are more soluble in water when free and combined with alkali, and, in general, possess less stable chemical properties than do similar bodies of higher molecular weight that occur commercially as soap stock.

72. Saponification of Palm Oil.—Palm oil, of which palmitin is the chief glyceride, finds only limited use as a soap stock in the United States. This oil is used chiefly as an ingredient of certain toilet-soap bases (for which purpose it is well adapted by its perfume) and to disguise the odor of rosin in soap of a high rosin content. In Great Britain and continental Europe, however, it replaces tallow to a large degree.

Sodium palmitate so closely resembles sodium stearate in its chemical properties that the statements concerning the properties of the latter salt are directly applicable to it. Palm oil saponifies very readily, owing to the high percentage of free fatty acids characteristic of the oil.

73. Saponification of Rosin, or Colophony.—Rosin when in a pure state consists of the anhydrides of the rosinic acids, chiefly abietic acid, $C_{18}H_{27}(CO_2H)$. On boiling, rosin is readily transformed into the acid, which combines with both carbonated and free alkali. Rosin may be *killed*, or saponified, alone or added after the kettle has been charged with tallow. The tallow may be saponified previously or both stocks may be killed together. The difficulty with which a pure rosin soap separates, or grains, in even a concentrated salt solution is the chief reason for its not being saponified alone. This is due to the fact that the specific gravity of rosin ranges from 1.07 to 1.10, while that of tallow is about .9. Soda ash may be used as the saponifying agent. The rosin soap thus made is frothy from the liberation of carbonic-acid gas, and as a result of the increased volume caused in this manner, much kettle space is required to work it. This saponification may be carried out by using a separate kettle and saponifying one or more charges at one time, pumping out the amount needed for each charge. However, where factory conditions are such as to warrant the use of soda ash instead of caustic soda, a considerable saving is possible, as is shown in the following approximate calculation:

EXAMPLE.—6,000 pounds rosin $\times .13 = 780$ pounds, approximately, of 74-per-cent. (see Table XII) caustic soda required for combination; $\frac{74}{60} \times \$1.75 = \$2.16$, cost per 100 pounds of 74-per-cent. caustic soda when price is \$1.75 per 100 pounds for 60 per cent.; $\$2.16 \times 7.8$ hundredweight $= \$16.85$, cost of 74-per-cent. caustic soda, required for combination.

$$2NaOH : Na_2CO_3 = 780 : x$$
$$80 : 106 = 780 : x$$

or

$x = 1{,}033.5$ pounds soda ash required for combination.

$1{,}033.5 \times \$.0009 = \$9.30$, cost of soda ash required for combination.

Caustic soda costs	\$16.85
Soda ash costs	9.30
Saving in alkali for 6,000 pounds of rosin	\$ 7.55

74. The alkali salts of the rosin acids are very hygroscopic and naturally readily soluble in water, and, as should be expected, make a very soft soap. They detract from the firmness of all soaps in which they enter. Rosin betrays its presence in the finished soap by the darker color and by its

characteristic odor and stickiness, which latter property is due to the marked affinity of the alkaline resinates for moisture.

This peculiarity manifests itself in the readiness with which poorly made rosin soaps sweat. The marked detergent property, ready solubility in either hot or cold, soft or permanently hard water, and cheapness of the alkaline resinates, make them an indispensable addition to the firmer tallow soap for domestic purposes. The characteristic odor may be ameliorated by the addition of suitable perfumes, and the stickiness may be reduced by the admixture in reasonable proportions of the tallow and rosin base. Highly rosined soaps become very dark on aging.

With rosin of the M and N grades of not more than 50 per cent. of the weight of stock, good laundry soaps of light color and excellent texture can be made by the method described later. These soaps are also free from sweating and rarely ever show any crystallization of salts on the surface.

75. The best proportions of tallow and rosin to employ depend primarily on the firmness of the tallow; that is, on the percentage of stearin present. This proportion also changes with the season, less being used in summer than in winter. A soft tallow cannot assimilate so much rosin as a firm tallow and the desired firmness of the finished soap be obtained.

It has been the custom of the trade to rate rosined soaps according to the proportion that the rosin bears to the fat stock by what is known as soapmakers' percentage. A 100-per-cent. rosin soap contains equal parts of tallow and rosin; a 50-per-cent. rosin soap contains 2 parts tallow and 1 part rosin; a 150-per-cent. rosin soap contains 1 part tallow and 1.5 parts rosin.

A soap properly made of these ingredients and in the proportion of 100 pounds of tallow and 50 pounds of rosin, with not more than 6 per cent. of soda-ash solution added in the crutcher, constitutes the standard high-grade settled rosin soap.

76. Saponification of Olive, Red, Corn, and Cottonseed Oils.—Olive, red, corn, and cottonseed oils possess

the same general chemical characteristics and behave in the same manner toward saponifying agents.

Olive oil was originally the basis of the soap known to Americans as Castile soap and on the continent of Europe as Marseilles soap. Pure olive-oil soap is white and very mild in its detersive action. It is composed chiefly, if caustic

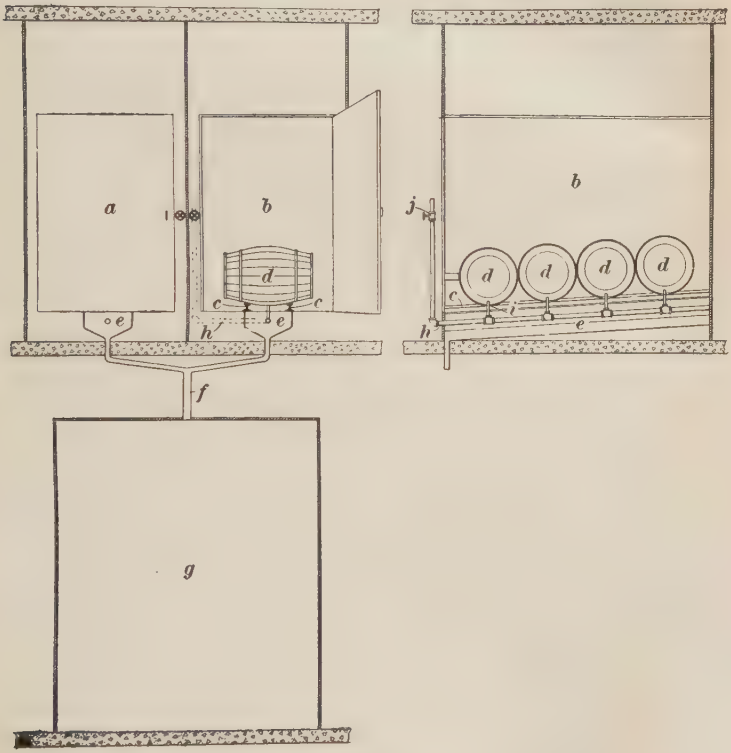


Fig. 8

soda is used to effect saponification, of sodium oleate. It is an excellent ingredient of a toilet-soap base and is especially adapted for use in the textile industry.

Red oil, or commercial oleic acid, being a stronger acid than carbon dioxide, can be saponified to the extent of about 90 per cent. with soda ash. Red-oil soap, sometimes called oleine soap, is practically identical in its composition and

properties with olive-oil soap, and is therefore equally adapted for the cleansing of textiles.

Cottonseed-oil soap stock, when in a clean condition and as free as possible from coloring matter, is identical in composition with red-oil soap and is adapted for the same technical uses. In connection with the use of cottonseed-oil soap stock, it should be remembered that it is simply soap, and unless in a very dehydrated condition does not admit of the yield common to all glyceride stock. It is simply an addition used because of its cheapness.

77. Removal of Stock from Containers.—The stock is received in barrels, tierces, drums, hogsheads, pipes, or puncheons. In some cases, factories are located so that it can be handled in tank cars. A typical melting room, two views of which are shown by Fig. 8, is generally located on the first floor and directly over tanks which receive the melted stock. It is usually a room with the sides and floor sheathed with iron plates and provided with two or more compartments *a* and *b* so that one charge may be melting while another is being set.

There is a track of inclined rails *c* in the center of each compartment on which the containers *d* easily roll. The gutter or pan *e* is placed directly beneath the container, and is also inclined in order that the melted stock will run forward and discharge to the pipe *f* which connects it with the stock tank *g*.

The inlet of this pipe has a strainer to keep out the bungs and foreign material that would block the pipes and pump. The steam line *h* with valves and swing nipples *i* is laid in the center of the track at intervals to accommodate the different size containers. The steam-control valve *j* is located outside the compartment.

When the charge has been set, blocked, and nipple adjusted to the bung of the container, the steam is turned on. In the case of fluid oils, it is not necessary to use any steam until all the fluid material has run out and then only for a short time. The length of time depends on the season. As the containers are removed they are examined with a light to make sure that they are empty.

78. Storage Tanks.—The best arrangement of storage tanks is to have a sufficient number to take care of not only the different kinds of stock but of the different classes of each stored. This calls for an assortment of both large and small tanks. These tanks are provided with closed steam coils so as to keep the stock melted and in shape for pumping and gauges on the sides graduated usually in 1,000-lb. units.

The stock received in the melting-out tank is allowed to settle. It is very necessary to store fats and oils as dry as possible to prevent decomposition. The melting-out tank is then emptied to the storage tank by a pump. The pump is fitted with a pet-cock by which samples can be drawn when the indicator on the tank shows the level at which water may be expected. As soon as water appears, the pump is shut off. This water is pumped to the first kettle taking a stock charge.

It is good practice to connect all the drips from the storage-tank coils into a small tank and examine this tank for indications of leaky coils. The tanks themselves will indicate leaky coils when they show more content on the gauge than the inventory carried on the tank. Once a week all the tanks should be tested for water and the stock kept dry.

79. Piping.—One of the most important features about all piping in a soap factory is that all lines from tanks or kettles to pumps be equipped with *steaming-out* lines. The piping is so arranged with stop valves that live steam can be turned into them and the entire line of communication made clear before any transfer of material is attempted. It is also just as vital that as soon as any pump has delivered its final charge that the entire line be again steamed out both ways, that is from pump to kettle and from pump to tank before the valves are closed.

It is not a rare thing to come into a soap factory on a morning in winter and find lines blocked because of the failure to have the lines steamed out. This steaming-out applies to all lines carrying soap or lyes.

MANUFACTURE OF SOAP
(PART 2)

PROCESSES OF SOAP MANUFACTURE

GENERAL REMARKS

1. The process of soap boiling consists essentially of effecting a chemical reaction between a fatty body and a caustic alkali or between a fatty or resinous acid and a carbonated alkali. The manner of bringing about this combination and the conditions under which the reaction is completed give rise to three general classes of soap-manufacturing processes, namely, boiled, semiboiled, and cold processes, whereby soaps, to which the same descriptive terms may be applied as well, are produced.

Boiled soaps are also called *settled soaps* when in process of manufacture they have been subjected to changes by means of which the soap is purified and the glycerine separated.

A *semiboiled soap* is one that has not been subjected to a graining process, but contains all the material added to the kettle. It is also called a *run soap*, which term, however, is without technical significance.

A *cold soap* is one made by the direct combination of the materials in the proportions in which they are to remain in the finished soap, the combination being effected without the aid of heat other than that required to bring the ingredients to the requisite temperature and that evolved by the chemical reaction.

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

The classification of processes just given is arbitrary and is not based on any essential chemical differences in the processes. The division is more mechanical than chemical and has reference chiefly to the time required, the artificial heat employed, and the mechanical apparatus necessary to a satisfactory operation of the process.

The production of a good boil of soap is dependent entirely on the judgment used by the soap boiler. His operations are due to the knowledge that experience has taught him. The successful boilers are keen observers, and, outside of one chemical test for free alkalinity, they depend solely on the looks of the kettle as it is boiling. Some boilers become so expert that they can estimate quite closely the free alkalinity of stock changes by the taste.

MANUFACTURE OF BOILED OR SETTLED SOAPS

BOILING-ROOM PROCESSES

2. Boiled Soaps.—The boiled soaps are the most important and constitute the class most generally manufactured and used. All laundry soaps, as well as the base for toilet soaps, are made by this process.

Before discussing in detail the manufacture of soap of this class, the essential features of the process as it is continued throughout the time required for its completion will be considered. There is arranged in Table I what may be called the outline of a boil of settled rosin soap. In this table is embodied an outline of the most important details of a boil of soap of this character. It is the soap most commonly made in the United States, and the procedure here outlined is the one generally followed.

In an elaboration of the treatment given the soap in the kettle will be discussed the directions and precautions to be observed, from the addition of the soap stock and alkali to the kettle, through the various changes to the transferring

TABLE I

OUTLINE OF A BOIL OF SETTLED ROSIN SOAP

Change	Material Added to Kettle	Saponification Agent	Graining	Disposition of Lye
First or stock....	Tallow, oil, grease.	18° Bé. caustic-soda lye.	Salt or brine	Drawn to empty tank and then to storage tanks for glycerine recovery.
Second, third, etc., wash changes...		18° Bé. caustic-soda lye to hold a free alkalinity of at least 20 per cent.	Salt or brine	Drawn to empty tank and then run to sewer.
First rosin.....	Rosin either in lumps or previously saponified scrap soap. Second rosin lye.	25° Bé. caustic-soda lye to hold a free alkalinity of 2 to 3 per cent.	Caustic-soda lye	Pumped to any first rosin change.
Second rosin.....	Boiled-up niger of previous boil.	25° Bé. caustic-soda lye to hold a free alkalinity of 3 to 4 per cent.	Caustic-soda lye	Pumped to any second rosin change.
Strong	Strong change lye.	Water or 3°–4° Bé. caustic-soda lye.	None	
Finish or settle water				None.
Niger				Boiled and pumped to any second rosin change.

I L T 322B—15

of the product to the crutcher and the addition of filling agents, to its final treatment in the drying room and its preparation for shipment.

3. The following soap-boiling process is carried out in factories where the maximum yield of glycerine is striven for. A yield of glycerine from 8 to 8½ per cent. is possible by following this method, when high-grade stock is used.

First change: Into a kettle from which the niger of a previous boil has been pumped on a second rosin change, run in water enough to cover 6 inches of the kettle bottom and boil with open steam. The stock pump is started and 18° Bé. caustic-soda lye is added simultaneously. Where grease, tallow, and oil are used, they are usually saponified in that order. When the saponification has started, noted by the swelling of the mass, the steam is eased off; only enough is used to keep the contents well mixed. This also serves to save room for the subsequent boiling. This change is complete when two boilings and tests show a free alkalinity of .20 per cent. Dry salt or brine is added until the soap becomes very *open* and the lye drops out clear.

Second change: Every effort is made to remove all the possible glycerine before adding rosin because in the best practice no rosin lyes are sent to the glycerine plant. Therefore, a number of these wash changes are made.

After the first lye has been drawn and sent to the glycerine-lye storage tanks, water and a small amount of 18° Bé. caustic-soda lye are added to the kettle and the whole mass brought to a good vigorous boil with open steam. Water enough is used to *close* or *flatten out* the soap and enough caustic lye to hold the alkalinity up to .20 per cent. It is grained with salt like the first change and the lye drawn and disposed of as before.

Third, fourth, and fifth changes: The number of these wash changes is dependent on the practice and experience of the individual plants. They depend also on the amount of water used on each change, the price of glycerine, the amount of exhaust steam available, the amount of glycerine-lye stor-

age, and the capacity of the evaporators. The water used is usually expressed in terms of the stock and varies from 250 to 450 per cent. A stock charge of 10,000 pounds will make a glycerine lye of 25,000 to 45,000 pounds. The procedure for these changes is the same as for the second change.

First rosin change: When the last wash change has been drawn, scrap soap, a small amount of recovered salt (usually high in sulphate), and enough 25 to 30° Bé. caustic-soda lye to *open* or grain the soap, is added. The alkalinity is kept up to 2 to 3 per cent. A second rosin lye is pumped in while the rosin is being added and the kettle kept at a good boil. This change is grained on the caustic lye, and, after settling, the waste lye is drawn to an empty kettle and run to the sewer.

Second rosin change: After the first rosin lye has been drawn off, enough caustic-soda lye of 25 to 30° Bé. is added to bring the alkalinity up to 3 or 4 per cent. A boiled-up niger is pumped in and the contents of the kettle vigorously boiled.

Strong change: When the second rosin lye has been drawn, open steam is turned on and enough water or 4–5° caustic-soda lye is added to flatten out the soap. When the mass is homogeneous and entirely flattened out, the steam is shut off and the kettle allowed to settle.

Finish or settle: As soon as the strong change lye has been pumped off, the soap is boiled up and usually small amounts of water worked in with slow boiling. This is continued until the soap boiler is satisfied that the soap has all the characteristics needed. The steam is then shut off and the soap allowed to stand until ready to frame.

4. Soap Kettle.—The soap kettle is made of steel plates of a thickness determined by its capacity. The plates are very carefully riveted and then calked to make them tight. Kettles are either square or rectangular; or cylindrical or slightly truncated. The first type is about 6 inches deeper in front than in back so as to provide a good pitch for draining, while the second type pitches to the center. Kettles of square or rectangular cross-section are more economical of space and make for a cleaner kettle room. It is necessary to brace the

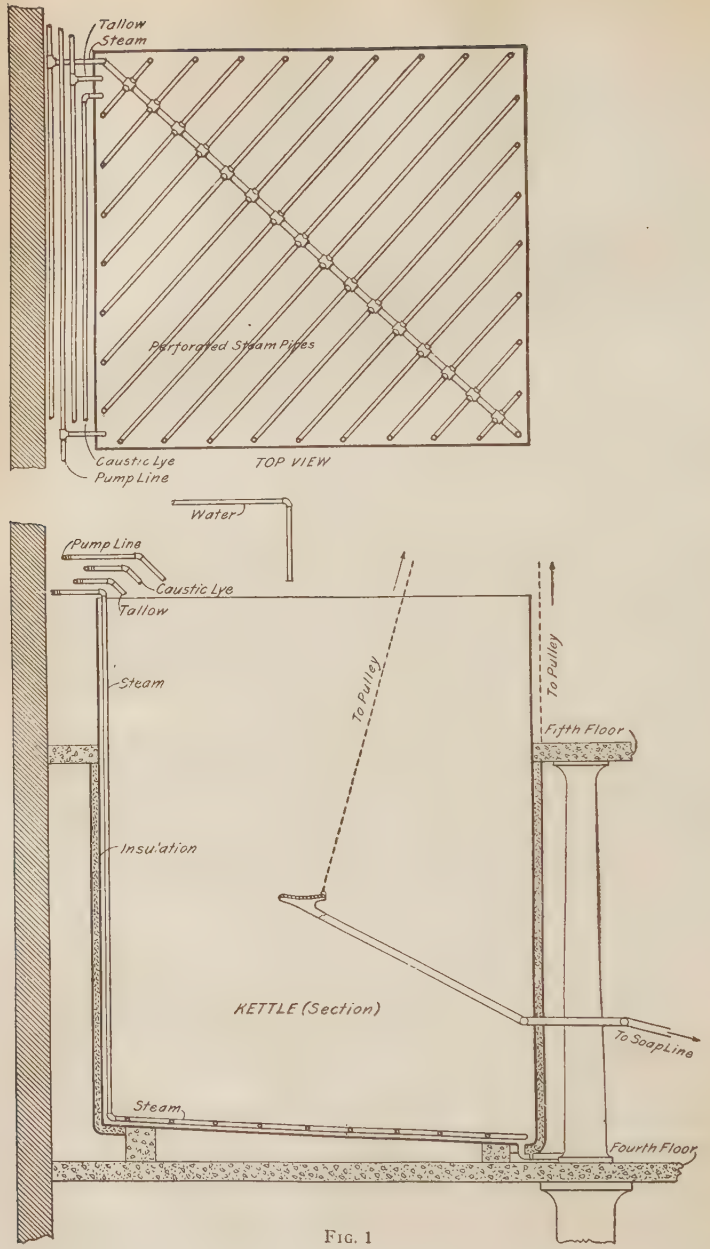

Tallow
Steam
Perforated Steam Pipes
Caustic Lye
Pump Line
TOP VIEW
Water
Pump Line
Caustic Lye
Tallow
Steam
To Pulley
To Pulley
Fifth Floor
Insulation
KETTLE (Section)
To Soap Line
Steam
Fourth Floor

Fig. 1

square and rectangular types with cross-rods, while the cylindrical types do not need them. For the manufacture of laundry soap alone, only open steam coils are provided. These coils are laid along the bottom. The steam header is extended down one corner of the kettle and the main arm is laid across to the other corner just off the bottom of the kettle, as shown in Fig. 1. This main arm has projecting arms of varying length which present a large heating surface. The arms have small holes drilled into them.

5. The steam-control valve is in the main line at the top of the kettle, and between it and the soap line a small vent pipe with a valve is fitted. At about the usual niger level, an opening into the soap line is provided and on the inside of the kettle this opening is fitted with a swing joint and pipe that can be lowered as the soap is being withdrawn.

On the boiling floor, the piping of each kettle is arranged for stock from the storage tanks, caustic-soda lye from the strong lye tank, steam, water and, a line by which lyes from any one kettle may be pumped into any other kettle. Connected to this line and also to the lowest part of the kettle there is a second line for drawing off the glycerine and rosin lyes. This line is also used for pumping nigers, strong change and second rosin lyes.

6. During the boiling, but especially for the settling, it is important as well as economical to conserve all the heat. Therefore, all the kettles are heavily insulated on the sides up to the boiling-floor level. Usually this insulation consists of 3 inches of magnesia-asbestos blocks wired on and covered with ½ inch of asbestos cement. This is covered with canvas and painted.

A very good layout of kettles is one that provides for an empty kettle at all times, that is, one in which no soap is made. In large plants there is one of these kettles for every ten. Into this kettle all glycerine and rosin lyes are drawn, and by watching from the top, the valves on the soap kettle being emptied can be closed at the first sign of soap appearing in the kettle into which the glycerine lye is being run. The lye can

then be sent to glycerine-lye storage tanks or in the case of rosin lyes direct to the sewer. If any soap has run in with the lye, it can be skimmed off and returned to the soap kettle. Fig. 2 shows the kettle-room arrangement, kettles, and piping plans.

7. The arrangement of the steam piping in a round soap kettle is a very important matter, as the successful handling of the contents of the kettle depends a great deal on the shape, diameter, and distribution of the coil. The diameter of the kettle will determine whether one or two open steam coils should be used. With a small kettle, one open steam coil or a crisscross jet in the center will suffice. This crisscross jet is shown at *f*, Fig. 3. With a kettle from 15 to 20 feet in diameter, a second open steam coil around the sides is necessary. The closed steam coil should completely cover the bottom of the kettle. Such a coil, with an open steam coil in the center, is shown in Fig. 4, in which *a* represents the central open steam coil, and *b* and *c*, respectively, the inlet and the outlet of the closed steam coil.

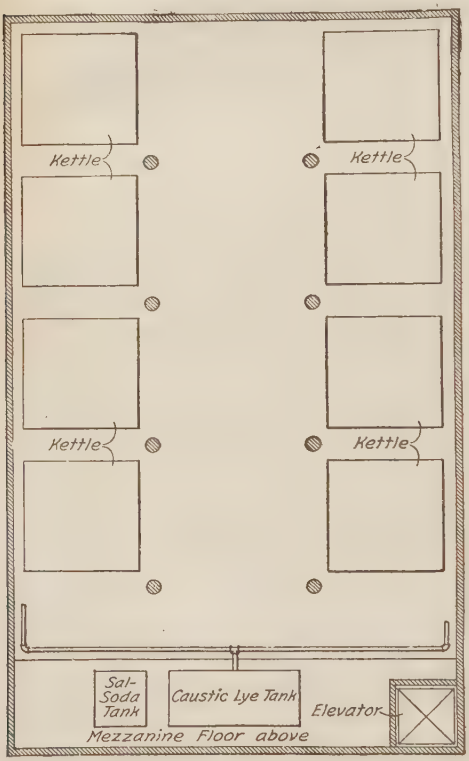


Fig. 2

8. The single pipe coil for closed steam, shown in Fig. 4, is more expensive than the jointed coil shown in Fig. 3, but

is not so liable to leak. The jointed steam coil is cheaper, more quickly and easily installed, and may be enlarged or repaired with only little trouble and expense. The only disadvantage is the greater possibility of leakage, because of the numerous threaded joints. The valves on both the open and closed steam coils should be within easy reach of the soap boiler, in order that the boiling process will be under control at all times.

9. The amount of stock that can be *killed* in a kettle of given capacity varies with the method of working. In general

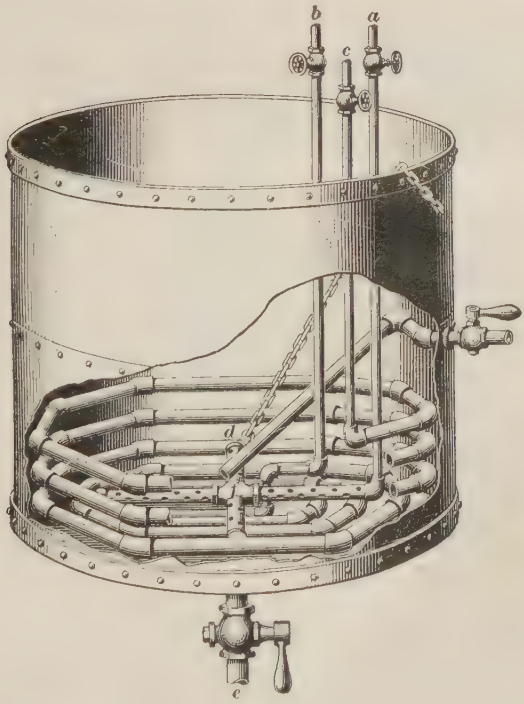


Fig. 3

terms, it may be stated that 1 cubic foot of space is allowed for every 12 pounds of stock to be saponified, or for every 100 pounds of stock.

10. Saponification or Stock Change.—In this discussion the following combination of stock and rosin will be used:

Stock and Rosin Ingredients	Pounds	Percentage
Tallow	28,000	90
Cottonseed oil or grease	3,000	10
		Percentage on Stock
Rosin, 36 bbl.	15,500	50

This combination will produce an excellent laundry soap. However, the proportions and ingredients may be modified, depending on the quality of soap desired. The kettle used is 12 feet 6 inches long, 13 feet wide, 16 feet deep at the rear end, and 16 feet 6 inches deep at the front end.

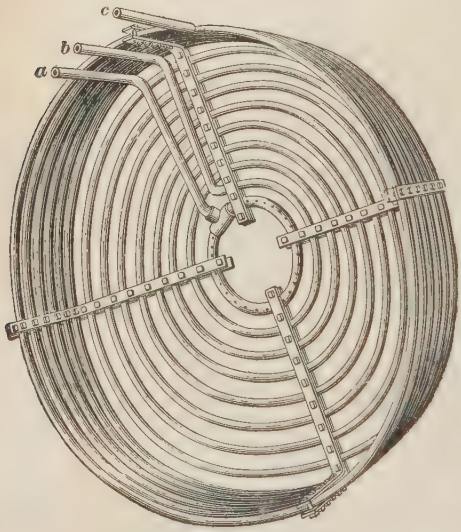


Fig. 4

11. With the variation prevailing in the quality of the raw materials, both organic and inorganic, used in the manufacture of soap, calculations cannot be made with accuracy. The amount of alkali theoretically absorbed by a given stock can be ascertained, however, and the quantity thus calculated can be used, but not infrequently will it be found that the soap will contain either a greater or smaller quantity of free alkali or more or less unsaponified matter, and unless a person has practical experience in soap boiling, it is almost certain that the soap will contain both.

Experience gained by working over the soap kettle is the final arbiter. The conscientious man will use the calculations

of theory and supplement them with his practical knowledge. It is better to have a small quantity of unkilled stock on the stock change and the alkali completely absorbed than to have an excess of alkali wasted in the stock lye.

12. Stages of Saponification.—The saponification of glyceride stock requires three stages for the complete formation of glycerine and the combination of the alkali with the fatty acids. While these stages do not admit of exact definition in the soap kettle, they manifest themselves in certain characteristic conditions, which are familiar to every soap boiler, namely, the emulsion formed on admixture of stock and lye, the pasty mass obtained on continued boiling, and, lastly, the final condition resulting from boiling the pasty mass with an amount of alkali sufficient for complete saponification. By means of chemical formulas, the three successive stages of saponification may be represented graphically:

Raw Materials:

	Stearin (tallow), $C_3H_5(C_{18}H_{35}O_2)_3$	Caustic soda: $3NaOH$
1.	Emulsion, $C_3H_5OH(C_{18}H_{35}O_2)_2$	Soap: $3C_{18}H_{35}O \cdot NaO$
		Soap: $C_{18}H_{35}O \cdot NaO$
2.	Pasty mass, $C_3H_5(OH)_2(C_{18}H_{35}O_2)$	Caustic Soda: $2NaOH$
		Soap: $2C_{18}H_{35}O \cdot NaO$
3.	Glycerine, $C_3H_5(OH)_3$	Caustic Soda: $NaOH$

The chief care is to add the stock and alkali simultaneously, with vigorous boiling, and in such proportions that, after saponification has started, the mass can be kept well open until the greater part of the alkali has been added.

13. While the alkali and stock are being run in together, the mass in the kettle must be kept homogeneous by vigorous agitation or by boiling with live steam. Unless maintained in agitation, too little alkali is liable to cause *bunching,* by which is meant local saponification enclosing a mass of unkilled stock. Vigorous boiling will disintegrate and distribute this mass. An excess of alkali grains the mass, thus throwing it, as it were, out of solution, whereby combination is retarded. By the time the total amount of stock has been

added, the greater part of the alkali should also be in the kettle, and boiling is continued, though less vigorously than at the beginning.

14. Care should be taken to avoid an excess of alkali, and at the end of the change it should be added in small quantities only and not until the strength of the quantity previously added has been absorbed. When the stock has been completely killed, the soap should slide freely from a paddle in large, transparent flakes. A small portion rubbed between the fingers should curl up smooth and dry and without any indication of grease. At this stage the contents of the kettle should boil smoothly, rising in the middle and descending at the sides, the appearance being very characteristic.

On the completion of saponification, the contents of the kettle has become a clear, homogeneous mass, in which is present everything that was added during this stage, namely, soap, glycerine, water, and some sodium chloride, sodium sulphate, and sodium carbonate, which were introduced as impurities with the caustic-soda lye. In addition, the mass contains more or less mucilaginous or albuminous matter that was present as animal tissue in the stock.

15. Testing for Free Alkalinity.—The free alkalinity of soap lyes is of the greatest importance. Every effort must be made to *kill,* or saponify, all the stock on the first change. It is just as important that the glycerine lyes be drawn as low in alkalinity as possible, because the more alkali they contain the more treatment they need before the evaporation can be started. A test for free alkalinity has been devised so simple that any man around the kettles can be taught its use in a short time.

When the soap boiler is satisfied that the condition of the kettle warrants a test, a sample of soap is taken out with a long-handled can, while the soap is boiling toward the top of the kettle. Parts of this sample may come from different areas of the kettle, but the locality near the caustic-lye inlet must be avoided as there is generally a small drip there. The can used has a small hole punched in its side near the bottom.

Dry salt enough to bring the sample to a good grain is stirred in. The can is kept tilted away from the hole. When it has stood long enough to drop a clear lye, the lye is drawn into a clean sample bottle by tilting in the opposite direction. The steam on the kettle is shut off while the test is being made.

16. The cylinder used has special etchings on the side so that at the usual 10 c. c. mark, the word LYE is placed beside the mark. At a mark 20 c. c. farther up the word WATER is placed in a like manner. A mark is put for each 2 c. c. and the half and full per cents. are etched on the sides. For all purposes a cylinder showing 4 per cent. alkalinity, will answer. The usual form of cylinder used is shown in Fig. 5.

Fig. 5

The test solution $\frac{N}{8}$ sulphuric acid is made and standardized in the laboratory. A bottle of distilled water and an alcoholic solution of phenolphthalein is provided. The acid and distilled-water bottles have quick-filling uncalibrated burettes for easy manipulation.

The test is made by adding the sample of lye in the clean cylinder to the lye mark, a few drops of phenolphthalein and water to the water mark, and shaking to mix well. The $\frac{N}{8}$ sulphuric acid is then added until the color is discharged.

The percentage of free alkalinity is then read directly on the cylinder. Each 2 c. c. of $\frac{N}{8}$ acid used equals .10 per cent. of free alkalinity.

The steam is turned on and when the soap has boiled through completely for a few minutes, the test is repeated. If it holds the same alkalinity it is ready for graining. If not, a small quantity of 18° Bé. caustic-soda lye is added and boiled through. This is repeated until the strength holds. By employing this easy test all guesswork in regard to free alka-

linity of lyes is removed. If the free alkalinity is too high, more stock is pumped in and killed.

17. Graining the Soap.—The object of graining is to separate the soap from the glycerine. This is done by adding salt or strong brine. The soap is insoluble in this solution, and on account of its lower specific gravity rises to the top while the lye carrying the glycerine and nearly all the salt falls to the bottom. The kettle is properly grained when a good bright lye drops. There are other salts that will grain; caustic soda and sodium sulphate are among these. Caustic soda is used on rosin changes. Sodium sulphate does not grain as clear as sodium chloride and it requires much more of it. Where reclaimed salt is used, the amount of sodium sulphate formed by the treatment in the glycerine recovery becomes so troublesome that when it reaches 20 to 25 per cent. of the salt, it is used on a first rosin change, and is thus eliminated from the system when that lye is run to the sewer.

Before adding the salt when graining, water enough is added to the kettle to make up the quantity of lye that it has been decided to make. This water is boiled into the soap. A good method of adding this water is to gauge it in time. The pressure from the city mains or from roof tanks that are held at a uniform level is constant enough for this. The instructions are usually given as 10 or 12 minutes of water. This is also done with caustic-lye solutions.

18. An excessive quantity of water in the kettle manifests itself by frothing, and under such conditions dry salt must be used. The nature of the stock used should also be considered. Tallow alone forms a soap that, at this stage, is of a characteristically firm consistency, although fluid.

Soaps made from cottonseed oil, red oil, olive oil, or rosin are very fluid, and from their consistency would seem to indicate the presence of an excessive quantity of water when such is not the case. Coconut oil makes a very fluid soap, and because of the large amount of salt required for graining, the latter should invariably be added in the dry state.

19. With the contents of the kettle boiling quietly, dry salt or saturated brine is added in small quantities at a time and thoroughly boiled through the soap until a portion taken up on a paddle coagulates or separates so that waste lye runs from it. The waste should be clear, of salty taste, and should not contain free alkali in excess of two-tenths of 1 per cent. This amount of free alkali in waste-soap lye is not perceptible to the ordinary taste.

The desired consistency of the grain is a condition arrived at by experience. The use of salt in excess of the amount required to produce this is not only wasteful, but also, if not thoroughly removed in the final settling change, tends to make the soap become fissured, or cracky, in the frames. The amount of salt added will partly determine the degree of hydration of the grained soap.

The more concentrated the salt solution in contact with the soap, the less water will be retained by the soap. With an insufficient quantity of salt, the soap will not be withdrawn entirely from solution. With such a condition, the contents of the kettle on cooling will not present a clean line of demarcation between the soap and the under lye, but there will be an intermediate zone of soft soap. Waste lye withdrawn hot from soap that has been insufficiently grained, will, on cooling, have the consistency of soft soap.

20. In boiling soap of the character under discussion the stock lye should not have a greater density than 13° Baumé, and will contain from 7 to 10 per cent. of salt. The soap is sufficiently grained when a waste lye of this character is withdrawn. It has been found by analysis that this is the lowest density that will remove the soap completely from solution; more salt than this is unnecessary and wasteful. The stock lye is the clearest and least discolored, and, owing to the high percentage of glycerine present, is the most valuable.

21. With the first appearance of a tendency to grain, the quantity of salt added previously should be thoroughly boiled through the soap, and each subsequent addition should be boiled through in the same manner before more is added.

When the desired grain has been obtained, the soap is boiled up to the top of the kettle, and the steam is turned off.

The time allowed for settling after graining depends on how fast the kettles must be worked toward the finish. Usually the kettle is rosined the first or second day after the stock change. This allows at least one glycerine lye to stand overnight. The other glycerine lyes may be drawn 2 hours after the graining is completed.

22. First Rosin Change.—A pure tallow soap has such poor lathering qualities that it needs rosin or oil to make it more soluble. Rosin and oil are used in laundry soap, but oil only, in toilet soap. The rosin is added either directly to the kettle or is saponified alone in another kettle and pumped in. Where the rosin is added directly, the barrels are generally rolled up to the kettle previous to the change being started and all the iron bands but one cut and removed. This is done so that by cutting the last band, the staves and heads fall apart and much time is saved. The rosin is broken into small pieces and shoveled into the kettle.

It is cheaper to use soda ash than caustic for this saponification. A 12° Bé. soda-ash solution is made and brought to a boil, the rosin is shoveled in as in a direct saponification and the whole mass kept boiling until no lumps of rosin are seen on the surface when the steam is shut off. Just before pumping, some dry salt is added to make it pump better. With the use of saponified rosin much less caustic lye is needed for this change. One thousand pounds of rosin requires about 150 pounds of soda ash.

A second rosin lye is pumped in on this change so that the excess of caustic that it contains can be used in dissolving the rosin and also to purify the soap by washing out the color and soluble impurities. The rosin changes are kept well *open* with caustic as very little salt is used. It is boiled thoroughly and always stands overnight so as to get out all the impurities possible.

23. Second Rosin Change.—The main object of the second rosin change is to insure complete saponification. The

boiled-up niger is added to fill up the kettle and reclaim all the good soap possible. All rosin changes are very tricky in their boiling and require all the skill of the soap boiler in getting a good mixing of all the ingredients. The steam is put on for a short while and the kettle watched very closely. The steam has a tendency to hold in pockets and break through with such violence as to jump out of the kettle. By putting on and shutting off the steam until it begins to break through quietly, a gentle boil may be had.

On the addition of alkali, as previously noted, the soap is well boiled through simultaneously with the addition of the rosin. Combination ensues quickly. The same care should be taken to insure the fullest absorption of the alkali, with the least amount added in excess to be discharged into the rosin lye.

During this change, combination is greatly assisted by keeping the contents of the kettle in a state of partial precipitation by the addition of caustic-soda lye. In the language of the soap boiler, this is termed either *graining the soap with alkali,* so called from the consistency that the soap assumes, or *keeping the soap open on alkali,* by which is meant not allowing the soap to *close* or *flatten,* or to lose its grainy appearance on passing into complete solution. *Opening the soap,* therefore, means partly precipitating it by the addition of a body in whose solution it is insoluble.

24. The rosin lye is nearly always very highly colored, with a depth of color depending largely on the quality of the rosin used. On the stock change, 31,000 pounds of mixed stock was killed. This admixture will carry well one-half its weight, or 15,500 pounds, of rosin -roughly, 36 barrels. After the withdrawal of the rosin lye there will remain in the kettle about 70,000 pounds of soap.

25. Strong Change.—The strong change is boiled on water if there is enough alkali left from the second rosin change, or with 4° to 5° Bé. caustic lye if it appears weak. The soap which has flattened out with the water will open very slightly so as to drop only a small quantity of slimy lye.

This change is boiled slowly, which tends to make the contents of the kettle homogeneous.

26. The purpose of the strengthening change is to complete the saponification and to discharge the salt, coloring matter, and other impurities retained mechanically by the soap. No salt is used for graining on this change. The 2 to 4 per cent. of salt commonly present in strengthening lyes represents the amount that has been retained mechanically by the soap and washed from it on this change.

The alkali wash promotes the discharge of the coloring matter, and completing the saponification of the last traces of unkilled stock also assists very materially in the development of the texture desired in the finished product.

27. Settling the Soap.—*Finishing* or *settling* the soap consists essentially in thinning the soap to the desired consistency with either weak lye or water. The water may be added during boiling or it may be derived from the steam condensed during this change. The strengthening lye from the preceding change is withdrawn and the soap is boiled up with live steam. Water is added in small quantities at a time until the soap is closed.

The boiling on the *settle* is done very slowly and may take all day to bring it into a condition that satisfies the soap boiler. Good soap can never be harmed by too much proper boiling.

Some free alkali is retained mechanically by the soap after the withdrawal of the strengthening lye. This amount is sufficient to impart a slight sharpness or alkalinity to the settled soap. It is claimed by some manufacturers that the soap should be settled in a perfectly neutral condition; others claim that the best results are obtained with a slight sharpness present.

28. The soap is boiled up to the top of the kettle and is then allowed to stand for about 6 or 7 days, during which time the contents of the kettle, by virtue of the different specific gravities, resolves itself roughly into two portions, namely,

the finished soap, carrying about 30 per cent. of water (this proportion, however, varying with the grain of the finish),

TABLE II

ANALYSIS OF SOAP DURING SETTLING PERIOD

	When Steam is Shut Off Per Cent.	After 12 Hours Per Cent.	After 60 Hours Per Cent.
Free $NaOH$	.15	.02	Trace
Free Na_2CO_3	.22	.13	.11
Salt	2.54	.77	.40
Water	45.58	32.82	30.40

and the niger, which carries considerably more water than does the supernatant soap, as well as the impurities and coloring matter settled from the latter. The settling change is a very important one, for on its proper operation depends the success or failure of the boil of soap. The length of time allowed to settle a boil, varies. It is best when permitted to stand a week. However, in the busy seasons it can be

TABLE III

ANALYSES OF NIGERS OF SETTLED ROSIN SOAP

	1	2	3
Water	59.14	66.29	55.86
Fatty and rosin anhydrides	30.41	23.27	35.83
Combined alkali	3.92	3.16	4.36
Free $NaOH$	.70	1.02	.86
Free Na_2CO_3	.56	.56	.58
Salt	2.34	3.24	1.71
Undetermined	2.93	2.46	.80
	100.00	100.00	100.00

crutched and framed on 4 or 5 days' settling. The settles of the same day are usually framed in the order of their temper-

atures, the coolest one being taken first. If one a day earlier than its schedule is needed, the coolest one is also framed first.

29. Niger.—The liquor from the settled soap is called the *niger*. It contains the impurities and constitutes from 20 to 25 per cent. of the volume of settled soap in the kettle. This proportion varies with the degree of hydration of the finished soap, the length of time allowed for settling, and the temperature of the mass. Analyses of the principal components of typical nigers are given in Tables III and IV.

The more thinly the soap is finished, the larger will be the niger, and the impurities of the finished soap, other things being equal, will be more completely settled into it. Care should be taken not to finish the soap too thinly, for the excessive quantity of water added to the kettle not only makes the finished soap softer, but leaves a large bulk of niger to receive subsequent treatment.

TABLE IV

ANALYSIS OF NIGER OF A TOILET SOAP

Water	70.83
Fatty anhydrides / Combined alkali	22.65
Free $NaOH$	.78
Free Na_2CO_3	.80
Salt	3.76
Undetermined	1.18
	100.00

30. On the other hand, a soap finished too closely, owing to the addition of an insufficient quantity of water, will separate the impurities very incompletely and yield a small niger. Other conditions being satisfactory, the longer the settling period, the more complete will be the separation of impurities, with the formation of a niger of proper volume. If, during this period great attention is not given and the soap is allowed to cool too quickly, which is often the case with a small kettle or with one exposed to the weather, especially in winter, separation of the impurities will be checked by a local or general cooling of the mass, and the niger will remain distributed unequally throughout the soap. This is overcome by insulating the kettle.

31. The settling change is not primarily a purifying change, but provides first for the production of a mass of a certain appearance and consistency, and when this is obtained and the proper conditions just noted are observed, the soap mass separates the impurities, thus forming the niger.

The soap mass is said to be finished fine or coarse, or, respectively, hard or soft, according to its degree of hydration. The condition described as fine or hard obtains when the soap taken up on the paddle and held in a slanting position falls from it in short, small flakes and cools rather quickly. The condition described as coarse or soft obtains when the soap falls from the paddle in large flakes and cools less quickly. The appearance and consistency must be learned by actual experience, by personal handling of the material itself. The process of clarification can be noted on the top of the kettle as soon as the final steam is shut off.

32. Filling of Soap.—The detergent qualities of soap are greatly increased by the addition of certain substances in aqueous solution while the soap is in a fluid state.

Borax and sodium carbonate are employed, bui the use of the former for this purpose is, as a rule, displaced by the cheaper alkaline carbonate.

As all surface water contains mineral salts, chiefly the carbonates and sulphates of lime and magnesium, it is necessary to neutralize these before the soap can exert any cleansing action. Insoluble soaps of lime and magnesium are formed by the combination of soluble soaps and the salts just mentioned, which impart the so-called hardness to surface water.

Sodium carbonate is a valuable addition to a soap, as a more economical use of soap is effected by its incorporation, as will be described subsequently. The carbonate effects the neutralization of mineral salts, thus leaving the soap to exert its legitimate cleansing action. The value of sodium carbonate to increase the detergence of soap was early recognized, as was also its property of hardening the soap, thus permitting the incorporation of more water than would be possible without its use.

Sodium silicate lends itself readily to incorporation with fluid soap, as it possesses very little detergent power. It is primarily a cheapener and imparts a smooth appearance to the finished soap, which becomes extremely hard on drying.

33. Sodium carbonate and sodium silicate are the chief filling agents. Their use in soap in large or small amounts is determined by the grade desired to be made and gives rise, respectively, to the terms *heavily filled* and *lightly filled*.

Mineral soap stock is a residuum from petroleum distillation that is frequently used in heavily filled soap. This stock

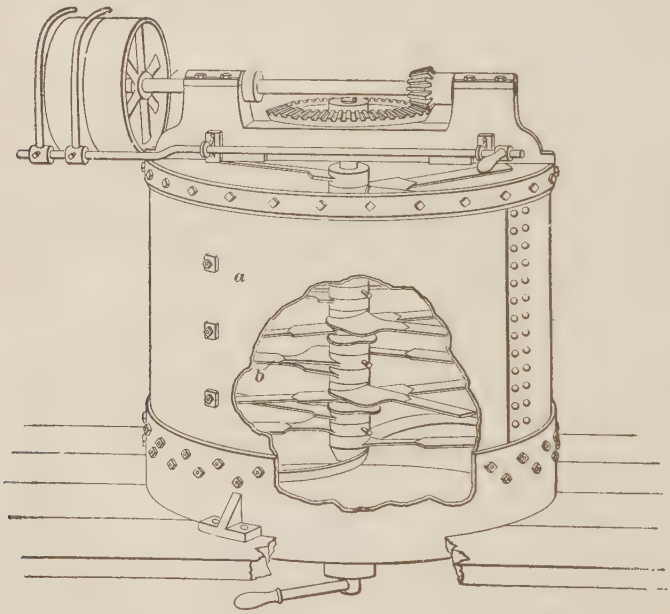


Fig. 6

imparts a smooth appearance to such soap, and thus counteracts the tendency of the mineral salts mentioned to grain the soap when added in large amount.

The limit to the use of filling agents is determined by the intelligence of the consumer. The incorporation in soap of filling agents is not, strictly speaking, an adulteration, so

long as the product is sold at a price commensurate with its quality.

34. Crutching the Soap.—For the incorporation of filling material into soap, the belt-driven crutcher is generally employed. There are three styles of this machine, each of which possesses several points of excellence.

Style A, shown in Fig. 6, consists of a cylindrical vessel *a*, in which is mounted a vertical shaft carrying a series of horizontal paddles *b*. These paddles rotate entirely within the body

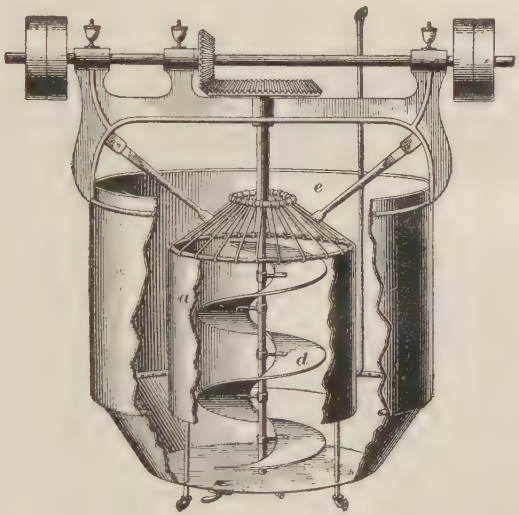


Fig. 7

of the soap, which remains practically stationary. The blades of the horizontal paddles may be so constructed, however, as to impart an upward movement to the soap. With a crutcher constructed as shown in Fig. 6, it is impossible to incorporate air into the mass of soap, as the mixing is done entirely within the body of the soap.

35. The distinguishing feature of the crutcher known as style B, shown in Fig. 7, is an inner concentric cylinder *a*, enclosing a broad Archimedean screw *d* mounted on a vertical shaft. Both the outer shell *e* and the concentric cylinder *a*

may be steam-jacketed or water-jacketed or fitted for both. This style is more commonly used without the steam jacket.

With this crutcher, the entire mass of soap may be moved from below upwards through the central cylinder by means of the screw *d*, and downwards between the outer shell *e* and the concentric cylinder *a*, or in the reverse direction, according as the belt is advanced or reversed.

36. Style C, shown in Fig. 8, is essentially the same as style A. The shaft of this crutcher is horizontal, with blades

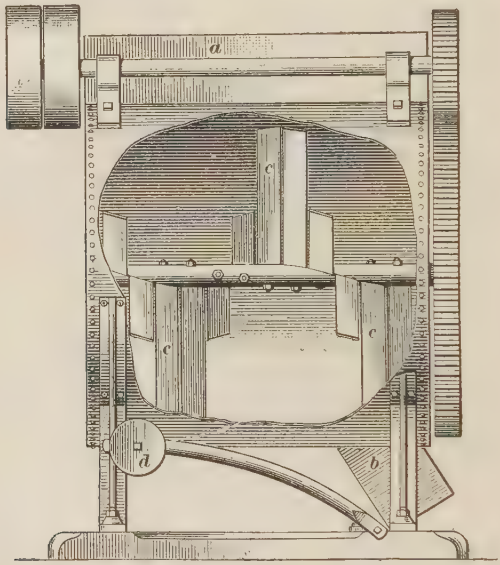


Fig. 8

of even or varying length mounted in screw-like fashion on it. Soap is pumped or dropped into the hopper *a* until the paddles *c* are covered to a depth of 2 inches. The crutcher is then started and run until the soap is crutched. The screw-like motion of the paddles works the contents of the crutcher toward the outlet *b*, which is closed by the counterpoise *d*. If the soap is not too thick, it will flow freely from the outlet *b*. If too thick, it is necessary to start the crutcher.

Each type of crutcher may be steam-jacketed or water-jacketed or both if desired. In factories that are not equipped with a separate remelter, this feature is essential. The steam-jacketed crutcher can then serve as a remelter. The capacity

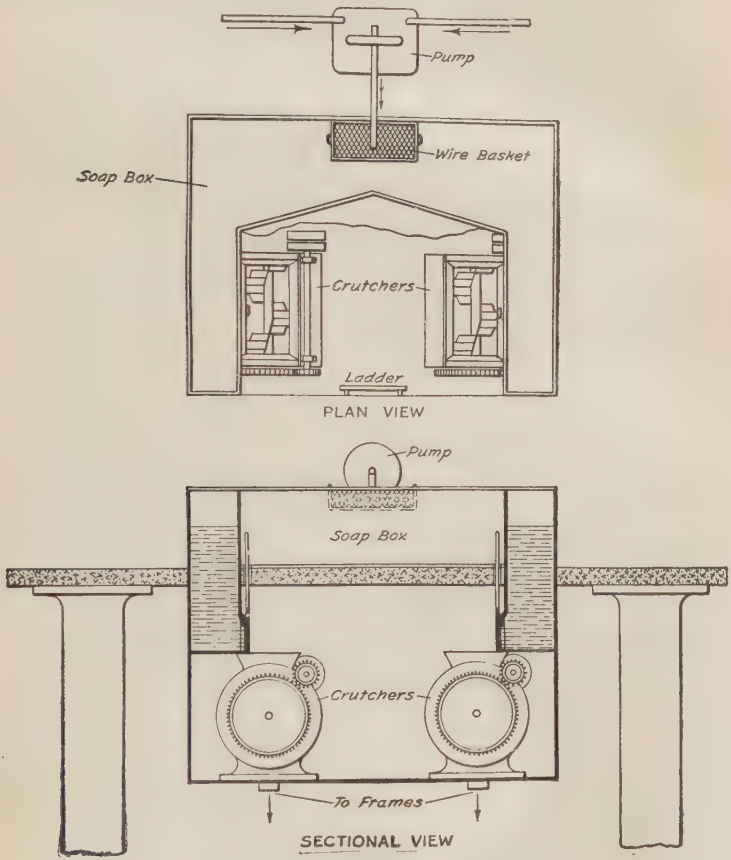


Fig. 9

of a crutcher is that of one frame, namely, 1,200 pounds. The crutchers are sometimes hung between floors in a cage or pit. It is the general practice to decide on a set temperature at which to drop each frame of the same class. A temperature of 142° to 145° F. is very good for the soap just described.

37. The use of the remelter is gradually growing less. It is much easier and cheaper to arrange the crutchers as shown in Fig. 9. This allows all clean scrap from the cutting tables to be added to the fresh soap going to the crutcher, where it serves a two-fold object. First, it is worked back into a finished form; and second, it cools the hot soap to the desired temperature. With well-insulated kettles, the soap crutching is seldom under 160° F. in winter and 170° to 185° F. in summer, and its temperature can be entirely controlled by the use of scrap so that water in the jackets is seldom used to get the temperature desired before dropping.

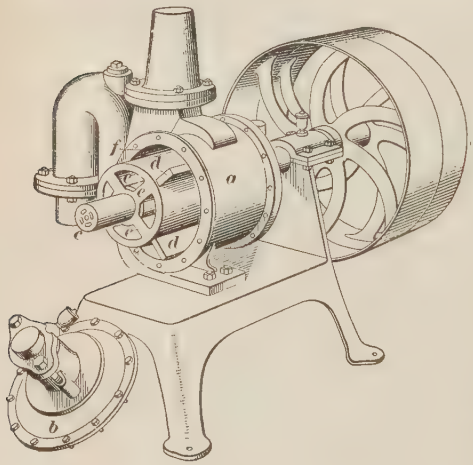


Fig. 10

Soap is pumped to the box, which is fitted with a heavy strainer, usually a wire basket. The amount of scrap that experience has determined to be proper, is added to the hot soap and stirred in with a paddle. As most of this scrap comes fresh from the slabber and cutting tables, it softens quickly. When the charge has been taken into the crutcher, the crutching is continued until the whole mass is homogeneous and shows no signs of the scrap soap used. It takes 10 to 12 minutes to accomplish this. This work proceeds so regularly that it is usually controlled by the clock.

38. Floating Soap.—With all other classes of soap, the crutcher is always filled well above the paddles or blades to exclude carefully all air. It is desirous to make ordinary laundry soap as dense in structure as possible. In making floating soap, however, this procedure is reversed and the

specific gravity is lowered by the incorporation of minute air bubbles.

To accomplish this, the crutcher is filled to within 6 to 10 inches of the top and covered, and the crutching continued until the soap has swollen to some predetermined height.

39. Soap Pumps.—The liquid soap is transferred to the crutcher by means of a pump. The pumps used vary some-

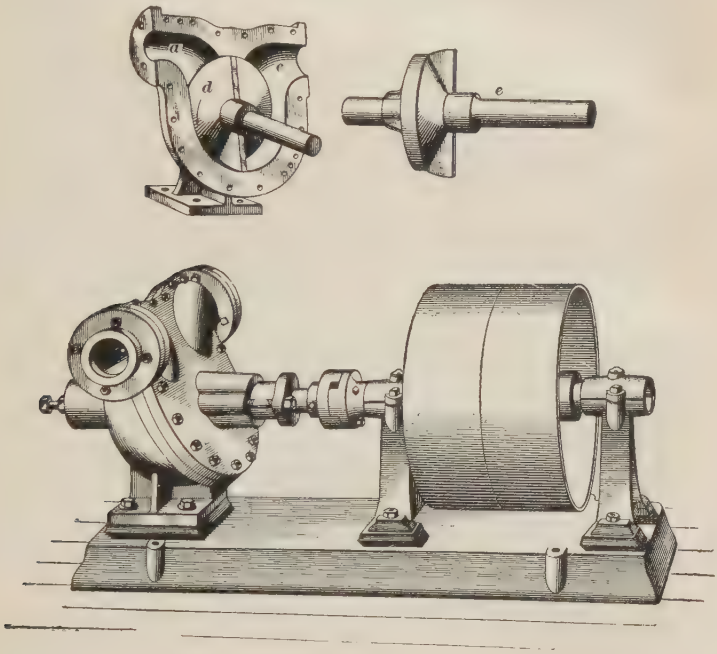


Fig. 11

what in construction, and only those most generally used will be described.

In the Tabor rotary pump, the working parts of which are shown in Fig. 10, *a* is the shell, or case, of the pump; *b* is the head that covers the end of the shell; *c* is the piston that carries the valves; *d* are the valves that pass through the piston in the ways *e*, and as the piston revolves, they pass in and out, back and forth through the piston, following the inside lines of the shell. The piston sets tightly against the shell at the

point *f*, between the point of suction and discharge. Rotating the piston creates a vacuum in the suction pipe, and the pump is thus set into operation.

40. The Hersey rotary pump, shown in Fig. 11, consists essentially of a cone-shaped casting, or piston, *d*, carrying blades, the whole being mounted on the end of a shaft *e*. The piston rotates in a specially shaped case, and when it turns in the direction indicated by the arrow, suction takes place at the orifice *a* and discharge at *e*. The reverse occurs when the piston is rotated in the opposite direction.

41. The Johnson rotary pump, shown in Fig. 12, consists of an outside shell *a*, with suitable parts *b* and *c* for connecting

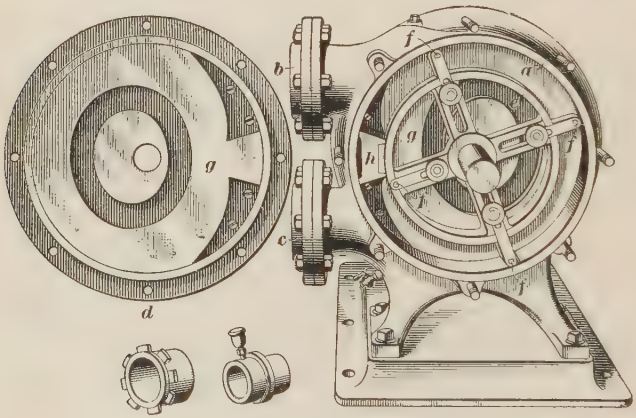


Fig. 12

suction and discharge pipes; two side plates, one of which is shown at *d*, with the cam *g*, and inside of all a circular casting, or piston, *e*, in which are held the piston heads *f* operated by the cam *g*. As the piston revolves, the cam *g* causes the piston heads *f* to move in and out of their ways, being at their extreme positions as shown in the figure. The block *h* separates the suction and discharge chambers.

42. The rotary type of pump is adapted for a variety of uses in the soap factory. Its simple construction, ease of

operation, and freedom from expensive repairs give it many advantages over the ordinary steam pump. The chief uses for a pump are to transfer stock and caustic lye to the soap kettle, the finished soap to the crutcher, and waste-soap lye to the glycerine refinery. Large plants are usually laid out so that as much work as possible can be done by gravity. As a rule, all glycerine lyes, caustic-soda lyes, and sal-soda solutions are handled in this manner.

43. On the discharge side of the pump there should be connected a steam pipe that will serve to blow out and clean the interior of the pump and the discharge pipe after use. As shown in Figs. 10 and 11 the pumps are provided with tight and loose pulleys, on the latter of which the belt may be shifted when the pump is not in use.

For pumping the soap from the kettle to the crutcher, the pump should be placed below the level of the draw-off pipe in the kettle, and the outlet, or discharge, pipe should be of slightly smaller diameter than the intake pipe. In this way gravity will aid the feed and provide for a steady discharge. The rotary, belt-driven pump represents a great improvement in productive economy over the old-time ladle and bucket as an instrument for transferring soap from vessel to vessel.

FILLING MATERIALS

44. Soda Ash.—The most valuable material to be added to laundry soap is soda ash. This material is introduced into the crutcher in the form of a saturated solution. The crutcher room is usually provided with a steam-heated kettle having an agitator for dissolving the soda ash as required. During the afternoon of the day previous to crutching, a quantity of solution sufficient for the entire boil of soap is made up.

When the arrangement of the factory permits, the sal-soda boiling tank is placed beside the caustic-soda lye tank on the soap-boiling floor. Another small tank is put on the crutching floor into which the sal-soda solution is drawn for use as needed. This serves to hold as much heat as possible in the

main solution. The amount of sal-soda solution is usually weighed for each crutcher charge of soap.

45. With a soda-ash kettle of given capacity, the quantity of soda ash and water necessary to produce a solution of the required density is easily ascertained by experience. The mixture is boiled with open steam to a density of 33° Baumé while hot. During the night the impurities in the solution, introduced by the soda ash, will have settled to the bottom and the solution will have cooled to a temperature of about 140° F., with the specific gravity increased to 36° Baumé. A solution lower than this in specific gravity should not be used in filling a soap.

The draw-off pipe should be placed 2 or 3 inches above the bottom of the sal-soda kettle, so as to avoid the removal of the settled impurities.

46. The quantitative properties of sodium-carbonate solutions above a density of 18° Baumé are determined at a temperature of 30° C. At a temperature of 15° C., solutions of the density shown in Table V (B) will crystallize, forming the hydrated salt, $Na_2CO_3 \cdot 10H_2O$, or $Na_2CO_3 10Aq$ (Aq. is the abbreviation for the word *aqua,* meaning *water*) as it is more frequently written, commonly known as *sal-soda.*

47. Concentrated solutions of sodium carbonate, when added in large amounts to any soap and particularly to soap made from soft stock, which, as known, sweats more readily than soap made from firmer stock, will soon cause the soap to effloresce. This is a most disagreeable property and detracts greatly from the appearance of the product. Also, when added in greater quantity than the soap can assimilate, the soda ash tends to grain the soap. With heavily filled cheap soaps, this condition represents the limit of the addition; soda ash and other filling agents possessing detergent properties then become adulterants.

48. Borax.—The addition of borax to soap is desirable, as this material is a mild alkali and possesses all the advantages of soda ash with none of its caustic properties. Owing to the

TABLE V

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE (LUNGE). (A) AT 15° C.

Specific Gravity	Degrees Baumé	Degrees Twaddell	Per Cent. Na_2CO_3	Per Cent. Na_2CO_3 10 *Aq.*	1 C. M. Contains Kg.	
					Na_2CO_3	Na_2CO_3 10 *Aq.*
1.007	1	1.4	0.67	1.807	6.8	18.2
1.014	2	2.8	1.33	3.587	13.5	36.4
1,022	3	4.4	2.09	5.637	21.4	57.6
1.029	4	5.8	2.76	7.444	28.4	76.6
1.036	5	7.2	3.43	9.251	35.5	95.8
1.045	6	9.0	4.29	11.570	44.8	120.9
1.052	7	10.4	4.94	13.323	52.0	140.2
1.060	8	12.0	5.71	15.400	60.5	163.2
1.067	9	13.4	6.37	17.180	68.0	183.3
1.075	10	15.0	7.12	19.203	76.5	206.4
1.083	11	16.6	7.88	21.252	85.3	230.2
1.091	12	18.2	8.62	23.248	94.0	253.6
1.100	13	20.0	9.43	25.432	103.7	279.8
1.108	14	21.6	10.19	27.482	112.9	304.5
1.116	15	23.2	10.95	29.532	122.2	329.6
1.125	16	25.0	11.81	31.851	132.9	358.3
1.134	17	26.8	12.61	34.009	143.0	385.7

(B) AT 30° C.

Specific Gravity	Degrees Baumé	Per Cent. Na_2CO_3	Per Cent. Na_2CO_3 10 *Aq.*	1 Liter Contains Grams	
				Na_2CO_3	Na_2CO_3 10 *Aq.*
1.308	34	27.97	75.48	365.9	987.4
1.297	33	27.06	73.02	351.0	947.1
1.285	32	26.04	70.28	334.6	902.8
1.274	31	25.11	67.76	319.9	863.2
1.263	30	24.18	65.24	305.4	824.1
1.252	29	23.25	62.73	291.1	785.4
1.241	28	22.29	60.15	276.6	746.3
1.231	27	21.42	57.80	263.7	711.5
1.220	26	20.47	55.29	249.7	673.8
1.210	25	19.61	52.91	237.3	640.3
1.200	24	18.76	50.62	225.1	607.4
1.190	23	17.90	48.31	214.0	577.5
1.180	22	17.04	45.97	201.1	542.6
1.171	21	16.27	43.89	190.5	514.0
1.162	20	15.49	41.79	180.0	485.7
1.152	19	14.64	39.51	168.7	455.2
1.142	18	13.79	37.21	157.5	425.0

higher cost, its use in soap manufacture is limited; with certain brands, only sufficient is used to justify in a measure the title given to the soap.

49. Sodium Silicate.—Next to soda ash, sodium silicate, commonly called *water glass* or *soluble glass,* is the most extensively used filling agent. Its consistency lends itself to ready incorporation with the semifluid soap. It possesses detergent power, and when used with due regard to the price of the finished soap, it is a valuable addition to the ordinary household soap.

Sodium silicate is made by fusing pure white sand and soda ash in a reverberatory furnace, such proportions being used that the resulting glass can be expressed by the formula $Na_2O \cdot 4SiO_2$. The resulting glass is broken into fragments and introduced into a digester that is already charged with an amount of water to yield a solution of any density desired, and high-pressure steam is then admitted. When solution is complete, the contents of the digester is run into barrels, in which shape it is received by the soap maker.

50. Sodium silicate is generally used at a density of 40° Baumé, in which condition it has the consistency of thick molasses, is transparent, and hardens quickly on exposure. At ordinary temperatures it will flow readily from the barrel. It must be in a fluid condition when used. In cold weather it may be softened by blowing steam into the barrel. If the head of the barrel is removed and the contents exposed to the air, those varieties deficient in alkaline strength will *jelly,* or separate free silicic acid through the displacement of the latter acid by the stronger carbonic acid of the atmosphere. This may be overcome by stirring up the mass with strong caustic-soda lye, thus effecting a combination of the silicic acid with alkali.

51. When intended for the use of soap makers, the sodium silicate has an average composition as follows: Water, 62.8 per cent.; SiO_2, 28.7 per cent.; Na_2O, 8.5 per cent. The more silicic acid the product contains, the more difficult it will be to dissolve it in water. The composition

of commercial sodium silicate, as it occurs in solutions of different densities to be used for different purposes, is variable, depending on the proportions of soda ash and silica used in the original charge and on the amount of water in which the fused mass is dissolved in the digester. There is practically no neutral silicate; that which is called neutral contains an excess of silicic acid, although it is not acid to litmus.

52. On aging, soap filled with sodium silicate becomes very hard. When well mixed with the soap, a reasonable proportion of sodium silicate greatly improves the appearance and enables a larger quantity of sal-soda to be carried without the efflorescence that would soon be produced without its use.

While sodium silicate possesses detergent properties, it is used primarily as a cheapener. By the use of suitable proportions of solutions of soda ash and sodium silicate, the quality of laundry soap is greatly improved. The soap is made more durable from the hardness produced by the crystallization of the salts; also the rapid drying of the soap is retarded.

When used in excess in cheap soap, the salts not only permit the absorption of a larger amount of water than would otherwise be practicable, but also, when used in soap made from soft stock, they impart a firmness that, without their use, would not be possible without having previously transformed the product into a variety of boiled-down soaps.

53. Miscellaneous Fillers and Adulterants.—Ground quartz, or silica, marble dust, mineral soap stock, a petroleum residuum, starch, and talc may be mentioned as fillers. They are adulterants pure and simple.

54. Perfuming the Soap.—With the best grades of laundry soap, it is common practice to add a small amount of either a single essential oil or a mixture of oils in order to produce a pleasant and lasting perfume. The quantity added is seldom in excess of 2½ pounds per frame. The selection of the oil or mixture of oils is best determined by experiment, the object being to choose an oil or mixture

of oils that will best counteract the resinous odor inseparable from rosined soaps. Too much care cannot be used in selecting a perfume for a soap, because, in many cases, the users identify the soap by its perfume.

55. Crutching the Filler and Perfume Into the Soap. The temperature best adapted to crutching depends largely on the character of the stock used in the soap and on the quantity and temperature of the filling material added in the crutcher. The temperature of crutching need not be so high for soap made from soft stock, because of its natural softness, as for soap made from firm stock.

If the crutcher is provided with a steam jacket, the soap can be easily kept at any desired temperature. Such devices, however, entail the use of a large amount of steam, and, moreover, for this purpose are not absolutely essential, but desirable. It is best and of great advantage to add the soda-ash solution at the same temperature as that of the soap, and when prepared as has been previously explained, it will be at the proper temperature when the soap is ready to crutch.

56. When ready to crutch, the swing-joint pipe is lowered a short distance below the level of the soap in the kettle and held in place by a chain, as shown in Figs. 3 and 4. The rotary pump is started and the crutcher is filled. When approaching the line at which the niger usually shows, the swing joint is watched very carefully and lowered a little at a time, just enough to keep the pump from sucking air.

The speed of crutching is best determined by experience. For a soap of the character under discussion, 80 pounds of sal-soda is run in and the mass crutched until fairy homogeneous. The sodium silicate is then added and crutched in. The perfume is added last, about 2 minutes before dropping, so as to avoid loss from the hot soap, and the soap is crutched until a portion removed on a paddle is perfectly homogeneous in texture and smooth in appearance.

Under satisfactory conditions, from 10 to 12 minutes is sufficient to crutch a frame of soap. With completely saponified soap that is pumped into the crutcher at a temper-

ature not exceeding 160° F. in winter and that carries a reasonable amount of filling, no trouble need be experienced in crutching. The primary conditions for satisfactory work are that the stock shall be completely saponified and the soap well settled. As to the soap being neutral or having a slight sharpness, there is a difference of opinion.

57. At the end of the crutching period, the outlet in the bottom of the crutcher is opened and the contents is emptied into a frame standing on the floor immediately below the crutcher. Where it is possible to operate two crutchers,

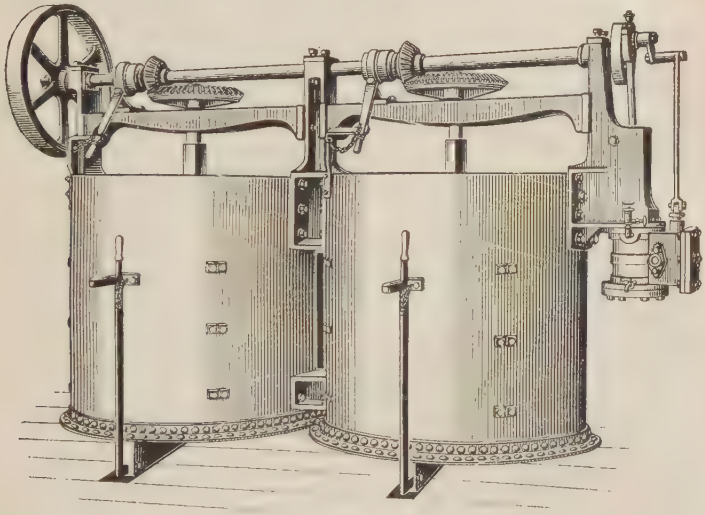


Fig. 13

mounted as shown in Fig. 13, the work is greatly facilitated, as the crutching can proceed in one while the other is being emptied, and vice versa. The man in charge of crutchers can always tell when the niger is reached. The appearance of the soap changes very decidedly; it becomes dark, thin, and streaky. By allowing it to flow across a trowel or paddle, the change is caught almost at once. The pump is shut off and the niger in the pump and line steamed back into the kettle. The niger is boiled up and pumped into any waiting second rosin change. The kettle is then ready for a fresh charge of stock.

FINISHING-ROOM PROCESSES

58. Framing the Soap.—The soap frame, shown in Fig. 14, has attained its present shape and size as the result of experience in handling soap at this stage of its manufacture. This frame consists essentially of an uncovered box with removable wood or sheet-steel sides, and with ends of wood or sheet steel set on a wooden bottom, which is mounted on truck wheels. It has a capacity of 1,000 to 1,200 pounds.

There are various styles manufactured, all with the single aim of producing a box that can be readily put together and taken apart, that will be durable, as light in weight as is

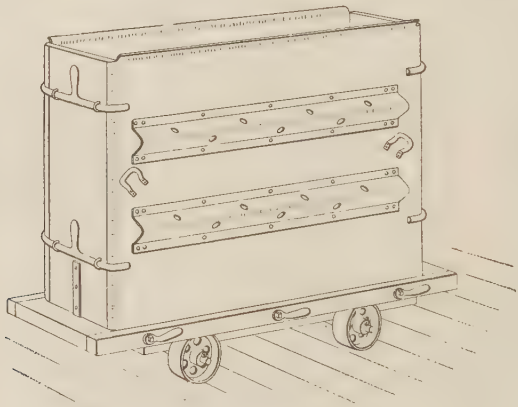


Fig. 14

consistent with strength, that can be easily moved about, and that will possess the most important qualification—tightness. The dimensions of the frame are variable and are determined, especially the width, by the size of the bar into which the slabbed soap is to be cut, it being the aim to keep the percentage of scrap at the cutting table as low as possible.

In the frame-room equipment, it is best to have an extra bottom for each frame. The sides of a frame may be removed after the soap has cooled sufficiently to permit this, and then mounted on the extra bottom. This is a most economical method, the usefulness of the frame being doubled, as the

original bottom carries the soap through the slabber and to the cutting table, by which time the original sides may be used to enclose a new frame of soap.

59. Previous to crutching, or as it proceeds, a sufficient number of frames are put in readiness. When the crutchers are operated in pairs, an empty frame should stand ready to receive its charge as the preceding one is being filled. The filled frame, with the soap smoothed down into the edges of the frame by means of a short paddle and heaped up longitudinally in the middle, is pushed into its stand in the frame room. Here it is allowed to remain for a varying period, usually from 3 to 5 days, which period is determined by the demands of the factory, the season, the character of the soap, and the temperature at which it was framed.

60. Before the steam-driven crutcher came into use, the soap was laboriously crutched in the frame with a *hand crutch.* The hand crutch, shown in Fig. 15, is still in use to prevent the filling material from settling to the bottom of the frame in soap that was crutched at too high a temperature; to distribute the material used to produce a mottle; or to distribute the reduction of temperature uniformly throughout the entire mass as cooling proceeds, thus preventing the separation of the softer from the harder soap.

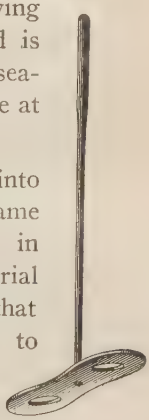


Fig. 15

With soap made from tallow, cottonseed oil, or grease, and rosin, and filled as has been noted, the sides may be removed from the frame on the second day after crutching. After removing the frame sides, the sides of the soap are scraped so as to remove any stains and blotches of adhering matter that may be present, and the soap is then ready to be slabbed.

61. Slabbing Machine, or Slabber.—The device known as the *slabbing machine,* or *slabber,* varies greatly in simplicity and cheapness of mechanical construction. It is a development of the old hand method of drawing a wire in parallel lines longitudinally through the mass of soap. In the machine

slabber, whether hand- or power-driven, the direction of application of the power is reversed, the frame of soap being forced through a series of parallel wires arranged on a framework to the height of the soap to be slabbed. The essential mechanical features of the machine slabber are shown in Fig. 16.

The power-driven slabber is automatic in action. The frame is run into the cage and the cutting head locked into place. The cutting head travels through the soap and returns, pushing

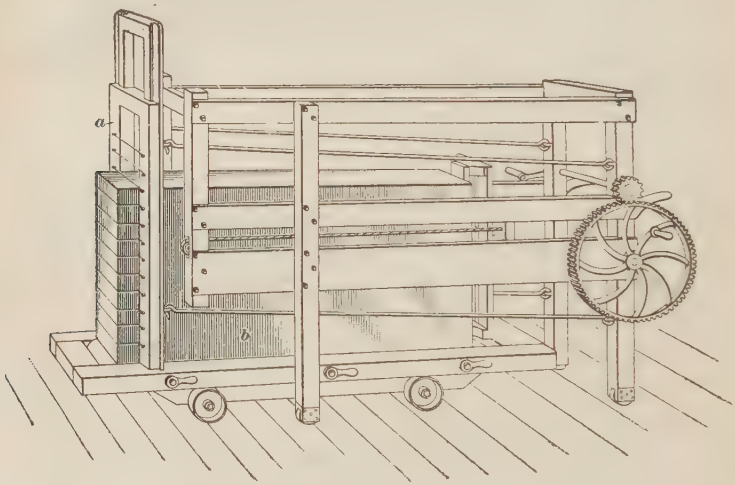


Fig. 16

the slabbed frame out of the cage when the slabber stops automatically.

62. Piano wire is the best for soap cutting. This wire is mounted on the frame head *a*, Fig. 16, in parallel rows at a distance apart corresponding to the width or height of the unpressed bars of soap. The frame of uncut soap is shown at *b*. By means of a key set in the sides of the frame head, the wires may be tightened or loosened as required. With soap that has stood for some time, it is often necessary to remove, for a short distance on both ends of the frame, the layer of soap that has become hardened. This permits the wires to enter the soap easily and to separate from it without the

abruptness that so often injures the wire; it also obviates undue stretching and breakage of the wires.

63. Cutting the Soap.—From the slabber the soap is moved to the cutting table, where it is cut into bars. The fundamental principle of all cutting tables is shown in Fig. 17. A slab is lifted from the pile *a* lying on the frame bottom and is transferred to the table *b*; it is then pushed lengthwise through one or two wires held in the cutting head *c*. In this way, the slab is cut into two or three narrower slabs as wide

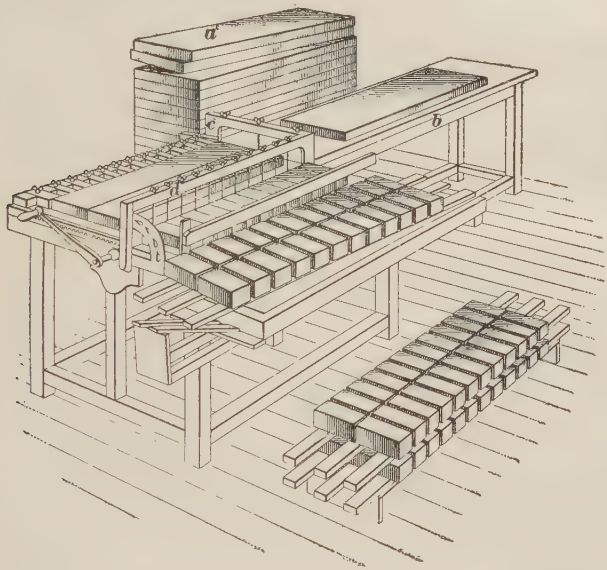


Fig. 17

as the single bar of soap is long. These slabs are then cut at right angles by another attendant to dimensions corresponding to the width and thickness of a single bar. The last cutting movement pushes the slabs through the wires in the cutting head *d*, when, as single bars, they are pushed on a rack supported by an extension of the cutting table. Here, by a slight upward and horizontal motion, the individual bars are separated so that air may circulate between them. The separate racks are placed on a truck until its full quota

has been received. The truck load is then taken into the drying room.

64. The slabbing and cutting of soap are purely mechanical processes and have for their object the division of the frame of soap into bars. The greatest care to be exercised at these stages is to slab and cut the soap to such dimensions that the amount of waste is reduced to a minimum.

Freshly cut soap is soft, sticky, and opaque, and, if properly crutched, should be homogeneous. It contains from 30 to 35 per cent. of water, according to the manner in which the soap was settled and the nature of the additions during crutching. In calculation, it is considered that 100 parts of glyceride soap stock will yield 150 parts of finished soap. The yield is less with rosin alone, and with some stock it may be as great as 157 per cent.

An analysis of pure settled soap at this stage presents the following data:

	Per Cent
Fatty anhydrides	61.80
Combined alkali	7.21
Anhydrous soap	69.01
Water	30.99
Total	100.00

65. Drying the Soap.—Aside from the processes in the kettle, there is no stage in the manufacture of settled soap that requires greater care in its operation than the treatment received in the drying room. While improperly dried soap may cause no great trouble in the press, it is subject to rapid deterioration in appearance, and the influence of this one factor on its ultimate distribution demands that its final treatment in the factory be given the closest attention of the soap manufacturer.

Previous to the introduction of the rapid-drying apparatus, the moisture in the exterior parts of the bar was allowed to evaporate spontaneously. By this method, the drying of soap was an extremely slow and unsatisfactory process, depending

largely on atmospheric conditions. A stove in a closed room was a great improvement. This primitive method, with its manifest disadvantages, was succeeded by a system of hot-air circulation by natural draft. Steam heat by simple radiation from pipes was also employed, and with the introduction of forced draft, the elements of the system of drying in use at present were established.

With laundry soap of good body, sufficient drying before pressing may be obtained in cool weather by standing the rack bottoms full of cut soap in front of an open window. It is necessary with this grade of soap only to get the surface *skinned over* enough so that the subsequent handling does not mar it and also prevents the soap from sticking to the dies of the press. However, in damp weather, and in summer, some artificial drying must be done.

66. Purpose of Drying Room.—The purpose of the drying room is to hasten the evaporation of water from the surface of the bar, so that there may be formed a thin crust of comparatively hard soap. This crust serves to retard further evaporation from the interior of the bar and allows the bar to be pressed and stamped without the soap adhering to the dies. Without the formation of this skin of firm soap, pressing and stamping cannot be done properly.

On cutting a bar of soap into halves, this superficial drying becomes plainly evident. The soap when removed from the drying room and after being pressed has a smooth, glossy, and translucent surface, which condition is in a marked contrast to that observed at the cutting table.

67. During the drying process, from 3 to 5 per cent. of water has been expelled entirely from the surface of the bar, while the interior contains the amount of water originally present, namely, from 30 to 35 per cent. The inequality of moisture contents between the exterior and interior parts of the bar partly explains the sweating to which settled soaps are universally susceptible.

This accumulation of moisture does not develop until after the bar is wrapped and packed. If a freshly pressed bar of

soap without wrapping were allowed to remain exposed to the atmosphere, it would dry, but would not sweat, assuming, of course, that the atmosphere has not attained the dew point. The moisture in the interior of the bar has passed through the hard surface into the atmosphere, and this process will continue until an equilibrium of moisture contents throughout the bar has been attained.

68. With soap wrapped and packed in a box, the conditions are entirely different. The tendency of the moisture to pass from the interior of the bar to the drier surface remains, but further evaporation from the exterior of the bar is checked. Here the moisture accumulates and softens the soap, which in turn adheres to the wrapper. This difficulty is overcome by using a parchment sheet between the soap and the outside wrapper. If the soap contains an excessive quantity of mineral salts, these are carried in an aqueous solution to the surface and on subsequent evaporation of the water form an incrustation. Boxed soap in storage should not be subjected to unnatural fluctuations of temperature.

69. Drying Soap by Forced Ventilation.—The mechanics of the modern soap-drying room represent more the adoption of a similar process employed in other departments of industry than they do a natural evolution from previous efforts in this particular field. The use of centrifugal fans in the production of artificial draft dates from the 16th century, but it was not until Stevens' experiments in the early part of the 19th century that the devices for artificial draft resolved themselves into the systems of ventilation known today, namely, the plenum and the vacuum, or, respectively, the forced and the induced, draft.

In connection with the drying of soap, ventilating fans may be divided into two general classes: the centrifugal fan, or blower, and the propeller, or disk fan. The former is more generally confined to ventilation by forced draft and is designed primarily for removing air under pressure. Fans of the disk type, shown in Figs. 18 and 19, are not adapted to plenum ventilation, where it is desired to move large volumes of air

quickly and under considerable resistance. They find extensive use and are very satisfactory for moving air under slight resistance, as under conditions met with in the ventilation of soap-drying rooms.

70. Both systems of ventilation, the plenum and the vacuum, are used in the drying of soap. The equipment of a drying room under the plenum system comprises, as a rule,

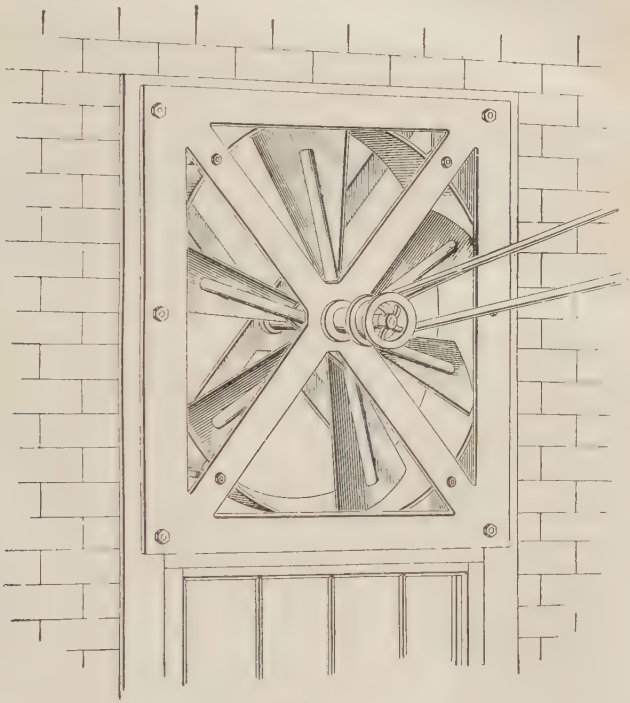


Fig. 18

a disk fan, two arrangements of which are shown in Figs. 18 and 19. In the arrangement shown in Fig. 19, the fan is operated either by a belt from shafting or by a direct- or belt-connected engine or motor and a sectional heater that consists of steam pipes enclosed in a sheet-iron case *a*, communicating with the discharge of the fan case *b*. Air may be forced through the heater and discharged at the desired temperature

into the drying room, or the fan may be interposed and air drawn through the heater and then discharged into the drying room. As the results produced are the same in either case, convenience of application will determine the arrangement.

71. With forced draft, the drying room is best constructed so that heated air enters at one end and leaves at the other, while freshly cut soap is introduced at one side, and, as the drying progresses, is withdrawn at the opposite side. The heater and fan may be placed at opposite ends of the room and the fan used to exhaust the warm and moisture-laden air. This

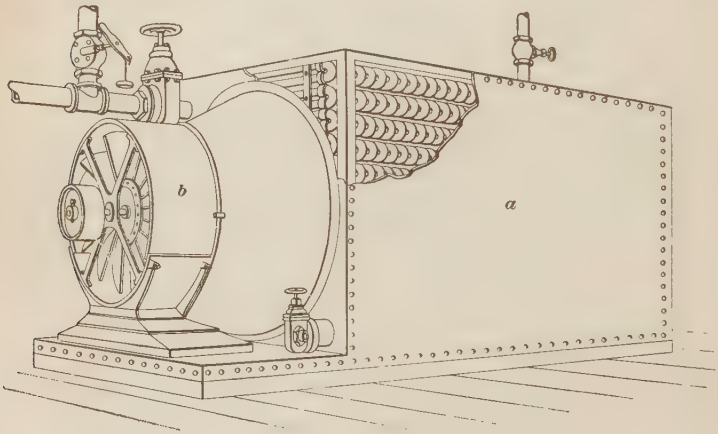


Fig. 19

arrangement presents an example of the vacuum system, or drying by induced draft. The combination of heater and fan shown in Fig. 19 is replaced with advantage by locating the heating coils at one end of the drying room or arranging them in rows throughout the drying room between the trucks of soap. The cheaper and simpler disk fan set in the framework of the wall, as shown in Fig. 18, is, with this arrangement for the drying of soap, equally efficient and satisfactory. The hot-blast drying apparatus shown in Fig. 19, although compact, may occupy valuable space. The exhaust-steam connections with the necessary insulation are simple and easily made.

72. Heating of the Drying Room.—By distributing the pipes of the sectional heater throughout the drying room in rows parallel with the trucks of soap and under openings immediately above for the admission of cold air, not only is a greater uniformity of the drying process obtained, but the use of the cheaper disk fan, which is admirably adapted for ventilation by exhaustion, is permitted. Exhaust-steam connections are made through the floor, and by means of suitably placed valves, exhaust steam may be cut off from any section, thus varying the capacity of the drying room at will.

73. In the drying process, air fulfils two functions: it carries to the moist soap heat necessary for the evaporation of the water and it serves as a vehicle for the removal of the vapor. The capacity of air for heat is very small, its specific heat being only .238, with water as 1; its capacity for vapor depends directly on its temperature and its relation to the dew point, naturally diminishing as the point of saturation is reached. With a rise of temperature, the capacity of air for moisture increases. It is estimated that air at 72° F. has a threefold greater capacity for aqueous vapor than the same volume at 42° F.; at 172° F., its capacity for vapor is more than eighty times as great. Increase of temperature thus means the more rapid formation of vapor, with a much greater increase in the capacity of air for absorbing it.

74. Requirements of the Drying Room.—The essential requirements of the heating and ventilating apparatus of the drying room are that a large volume of air be provided at the required temperature and that this be maintained in rapid circulation. A comparatively low temperature, namely, 90° to 100° F., is productive of the best results. Air maintained at a temperature in excess of 100° F. for a long period causes the soap to undergo an appreciable softening, with more or less discoloration.

The temperature at which soap will melt depends primarily on the nature of the stock and the proportion of water present. In the drying of *green* soap, it is desirable that the currents of warm air circulate lengthwise of the bar, in order that the

largest extent of evaporative surface may be exposed and the drying process thus hastened. The duration of the drying period is easily learned by experience, from the appearance of the bar; it varies from 6 to 12 hours.

75. Pressing of Soap.—Hard soap was originally sold in the United States in bulk. Later, the soap was cut into bars and packed, with the wrappers in bulk, in a box, the retailer himself wrapping the soap as sold. Under present conditions, however, the freshly cut bar is pressed, stamped, and wrapped.

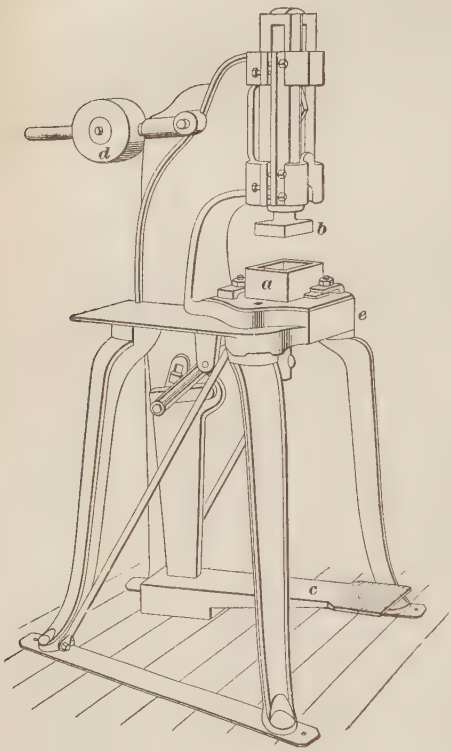


Fig. 20

In Fig. 20 are shown the essential features of a foot-power soap press. This machine is arranged so that the operator can deliver a sudden blow to the cake of soap placed in the die box *a*. The thumb and forefinger of the right hand are used to place the soap in this die box. An operator on a press of this kind will press thirty bars per minute. To prevent soap from adhering to the die *b*, the cake is placed lightly on a bunch of waste saturated with brine or a mixture of vinegar and water that is usually located at the right of the die box *a*. After the blow has been delivered by the right foot placed on the lever *c*, the upper die *b* is lifted by the counterpoise *d*, which also serves

to add momentum to the force of the blow, and a lever action lifts the pressed bar out of the die box *a*. The bar is then transferred, by the left hand of the operator, to a table at his left. The foot-power soap press is built in a number of styles, some being partly operated by steam, as shown in Fig. 21.

76. Steam Foot-Press.—The steam foot-press, Fig. 21, is provided with a steam cylinder *a*, the piston *b* of which is

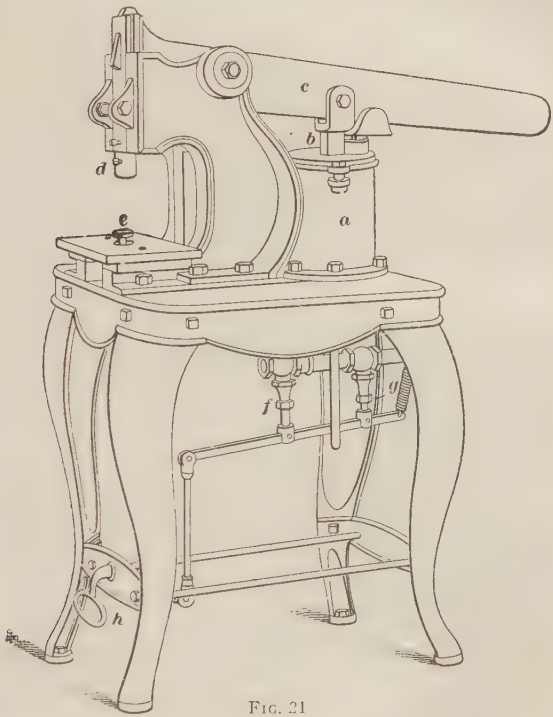


Fig. 21

directly connected with a lever *c* that controls the dies *d* and *e*. A system of valves is arranged at *f* and *g*, from which points, by a slight pressure of the foot on the treadle *h*, steam is admitted to the cylinder *a* and a quick, powerful blow is given to the soap placed over the die box, the lower die *e* of which is elevated as shown. The lever returns instantly, withdrawing the upper die and elevating the lower one, from which the cake

of soap is removed by the left hand of the operator. With rapid work, upwards of 1,500 cakes an hour can be pressed on a machine of this type. This kind of press is not used

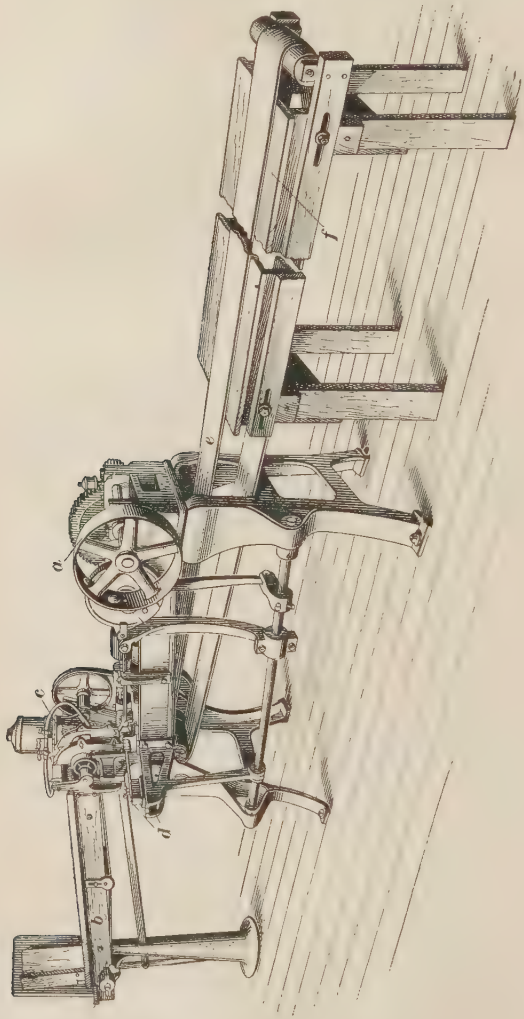


Fig. 22

extensively at the present time; it is replaced by more modern machines, which are entirely automatic and give a much higher output.

77. Automatic Steam-Power Soap Press.—The belt-driven, automatic soap press is a direct development of the old foot-power press, and arose from a demand for greater rapidity of operation. Several styles are on the market, with a guaranteed capacity of from 60,000 to 75,000 cakes per day of 10 hours. They are perfectly automatic in their action, require but little attention, and for a factory producing upwards of 400 boxes of soap per day, such a machine is a safe purchase.

The more improved forms admit of interchangeability of the dies, thus permitting the soap manufacturer to use any die that he may have in stock. Thus all the brands of a single factory can be pressed on the same machine, with no longer time required to change the dies than on the old-style foot-press. On the high-speed presses, a dilute solution of acetic acid (3 to 4 per cent.) is allowed to drip on the dies to prevent sticking.

78. In Fig. 22 is shown one of the latest forms of steam-power soap press. To describe it briefly, power is applied to the pulley *a*, which in turn operates the feeding belt running on the surface of table *b*. This belt carries the cake of soap to the drop box *c*, down which it falls between the two dies impelled in a horizontal plane at *d*. The cake of soap as it falls down the drop box *c* is caught between the two dies, pressed, and dropped on the belt *e*, which carries the pressed bar to the wrapping bench *f*, where it is wrapped and then packed in boxes.

79. In Fig. 23 is shown a three-die rotary soap press. This machine consists of double cylinders *a* and *b* placed end to end, in which rotate cams that automatically bring together and withdraw horizontally two dies that meet in their corresponding die box, of which three are arranged 120° apart. The dried soap from the racks is placed on the feeding belt *e*, from which each bar is singly moved forwards to the die by a *finger* on the chain belt passing over the pulley *d*, to which power is applied at *c*. A set of dies is shown at *f*. The pressed soap is dropped on the belt running in the box *g* and is conveyed to the wrapping bench.

80. Wrapping by hand is done in small establishments. It has been superseded in the larger ones by automatic power machines, the soap coming from the presses feeding directly to

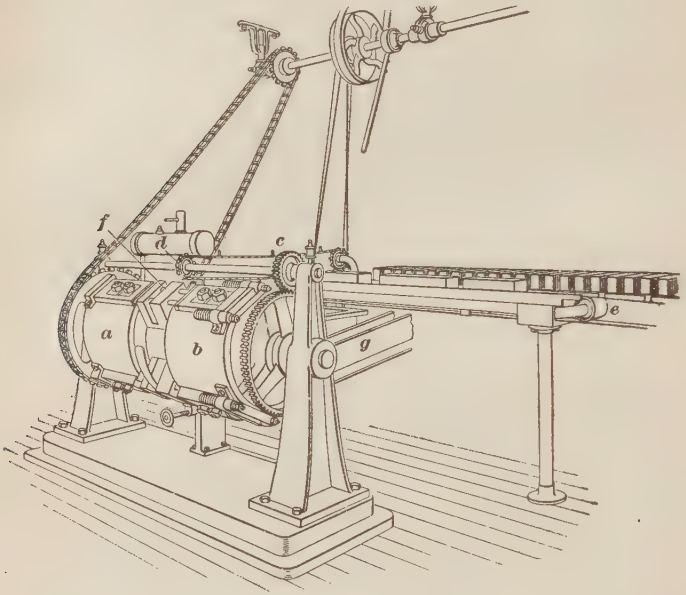


Fig. 23

belts that supply the wrapping machines. The press just described requires two wrapping machines. The wrapped soap is packed into the box as it leaves the machine.

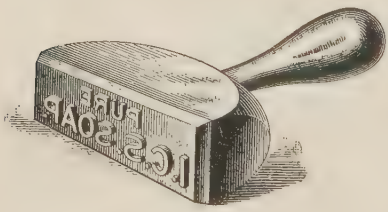


Fig. 24

Among the many advantages possessed by automatic soap presses are chiefly the perfect work, capable, at a maximum speed, of 150 bars per minute; the regulation of the pressure to suit the character of the soap; and the insurance of safety to the operator from loss of fingers. The automatic power press of the capacity stated will do the work of five foot-presses with one-third the labor.

81. Soap Dies.—The kind of die to be used is determined by the kind of soap to be pressed. The function of a die is twofold: it forms the yielding mass of soap into a definite shape and imprints on the cake thus formed, in either elevated or sunken letters, or both, usually the brand of the soap and the name of the manufacturer or vender.

The earliest form is the hand stamp, shown in Fig. 24, by means of which the brand or maker's name is impressed on the freshly cut bar.

82. The second form is the box die shown in Fig. 25. In this form of die, the mold feature is introduced in pressing the soap from above and below in an enclosed space called a *box*. The upper die *a* and the lower die *b* fit closely to the interior of the box *c*. They are so adjusted with the press as to cause their respective downward and upward movement at a separating distance corresponding to the thickness of the pressed bar, which dimension the thickness of the unpressed bar closely approximates. There is thus insured such a distribution of the soap in the mold as to fill every part of it.

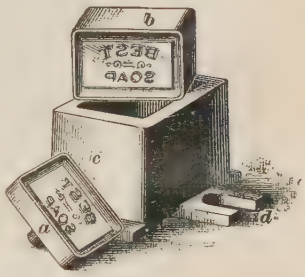


Fig. 25

The same box and dies may be used for different brands, by means of detachable name plates. In fitting the box to the bedplate of the soap press shown at *e*, Fig. 20, by means of the shanks shown at *d*, Fig. 25, care should be taken to insure a perfectly vertical motion of the upper and lower dies; otherwise, they will rub against the interior sides of the box, with the result that the accuracy of the die will soon be destroyed.

83. In the molding and stamping of milled soap, dies of a different construction must be used because of the greater firmness of soap of this character. A powerful and sudden blow must be delivered, and the construction of the die must be such as to expel all surplus soap from the cavity, instead

of, as in the more yielding laundry soap, forcing this surplus into every part of it.

The pin, or shoulder, die is so called from the use of pins and sockets to guide the upper and lower dies, thus preserving

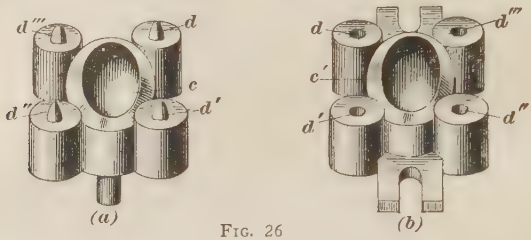


Fig. 26

their accuracy. The term shoulder has reference to the base supporting and receiving the four pegs. As shown in Fig. 26, this third form consists of two dies, (*a*) being the top die and (*b*) the bottom die, without a box, each forming the face and one-half of the cake. The edges *c* and *c'* of the dies strike together, thus forcing out all surplus soap. The guide pins *d*, *d' d''*, and *d'''* of the top die serve to guide it squarely

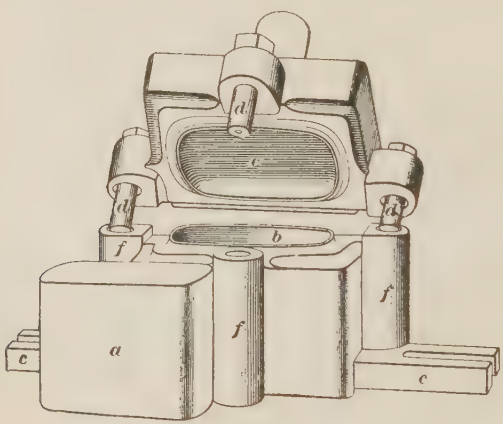


Fig. 27

on the bottom die. The shoulders of the bottom die, receiving the guide pins in the corresponding holes *d*, *d'*, *d''*, and *d'''*, bear the force of the blow, and preserve the cutting edges *c* and *c'*. These dies are also made with removable panels,

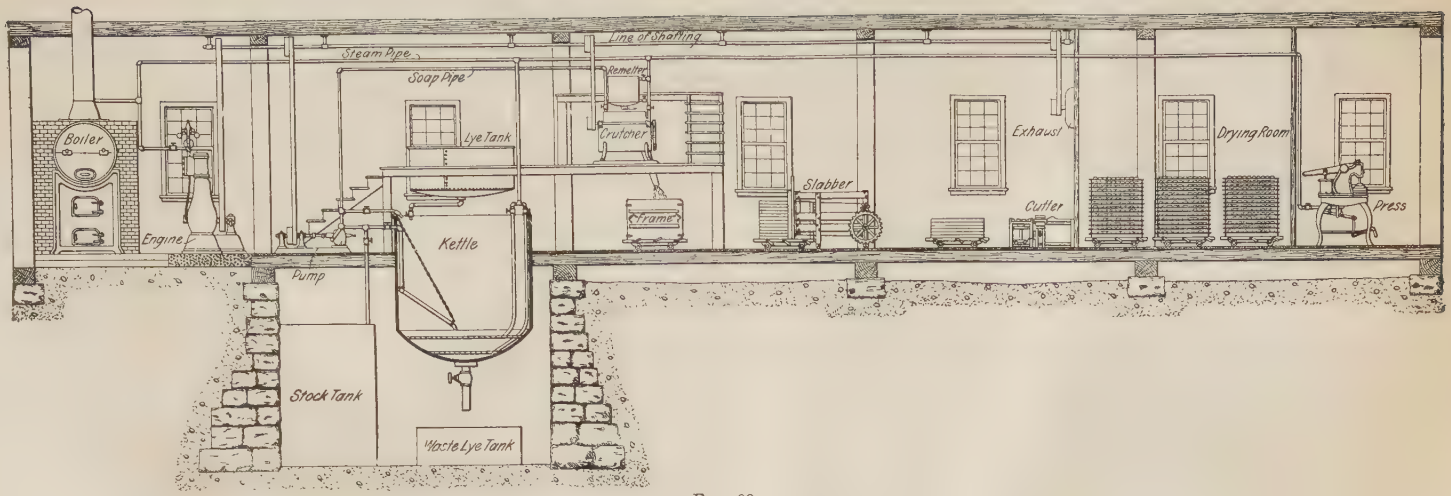

Line of Shafting
Steam Pipe
Soap Pipe
Remelter
Boiler
Lye Tank
Crutcher
Exhaust
Drying Room
Slabber
Frame
Cutter
Press
Engine
Kettle
Pump
Stock Tank
Waste Lye Tank

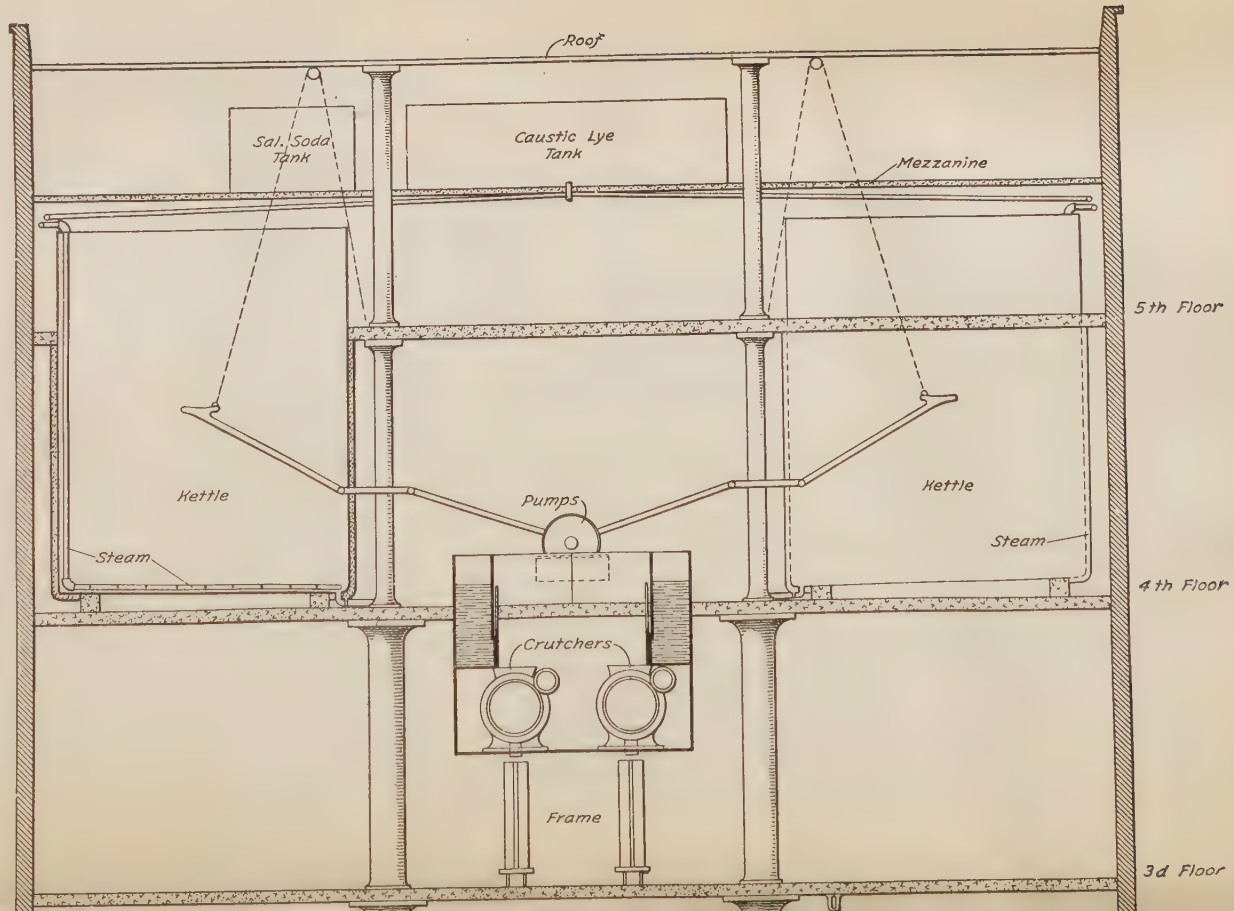
Fig. 28

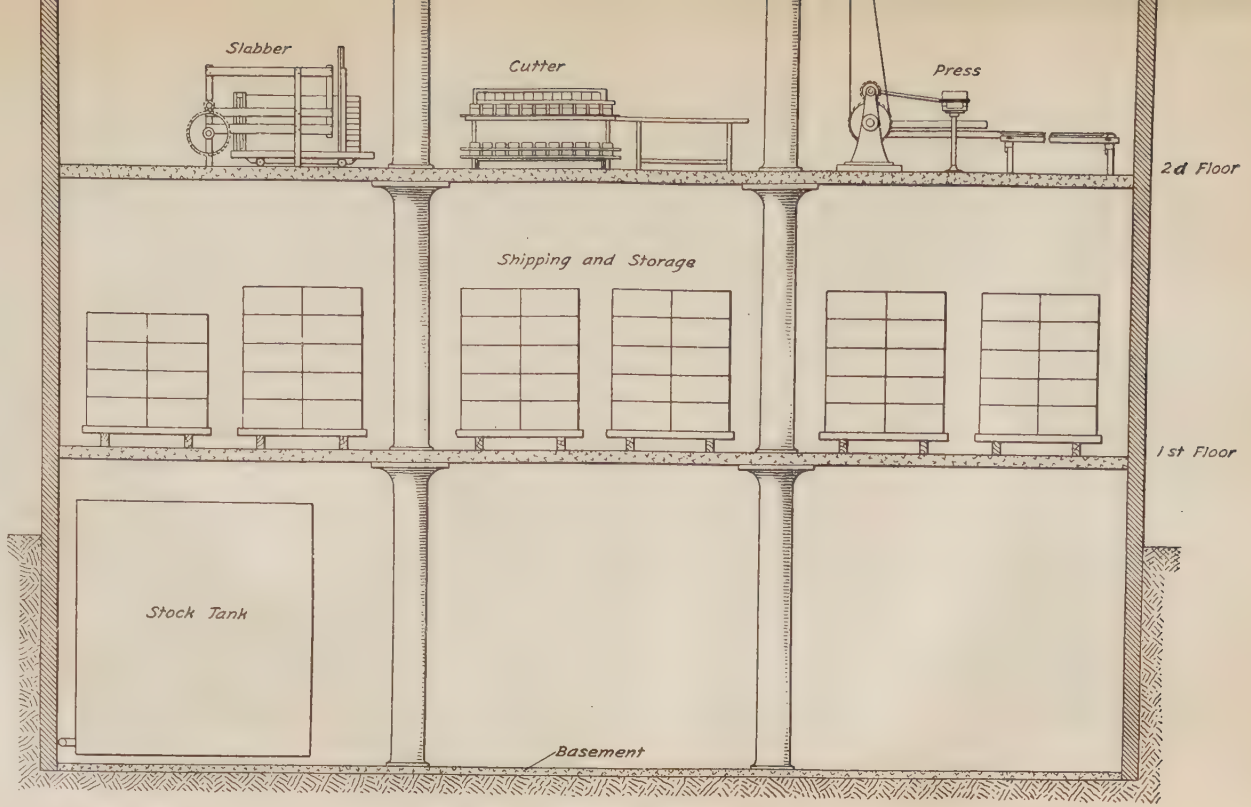
or name plates, thus permitting a number of brands to be stamped with the same die by inserting a different name plate in the base of the bottom die.

84. The fourth form is a combination of the pin, or shoulder, and box dies, and in addition to possessing the qualities of each, it admits of the pressing of cakes of different thicknesses and weights by virtue of the removable lower die placed in the box. As shown in Fig. 27, *a* is the removable lower die, which is made in varying heights so as to produce a bar of corresponding thickness. It fits into the box *b*, which is fastened by the shanks *c* to the bedplate of the presses shown in Figs. 20 and 21. The guide pins of the top die *e* are shown at *d*, and shoulders of the lower die at *f*.

The dies are made of gun-metal alloy or rolled brass. They should be substantially made with all moving parts carefully fitted. The engraving should be so executed, with letters or figures of uniform bevel, as to produce in the soap clear-cut and even characters, more especially when these are in relief. The workmanship of the die is shown at once in the appearance of the pressed soap. A good die greatly improves the appearance of an inferior product. Toilet soap is stamped on foot-presses, the automatic press having not as yet proved satisfactory for stamping milled soap.

85. Plans of Two Types of Soap Factory.—Two general types of soap factory are shown in Figs. 28 and 29, Fig. 28 showing all the equipment on one floor, and Fig. 29 the gravity plan as used by the larger plants, by which the soap is boiled on the top floor and finished on the way down. From these two plans, in conjunction with the methods and apparatus described in the preceding articles, each operation may be traced.


Roof
Sal. Soda Tank
Caustic Lye Tank
Mezzanine
5th Floor
Kettle
Pumps
Kettle
Steam
Steam
4th Floor
Crutchers
Frame
3d Floor



I L T 322 § 25

SECTION OF 5=STORY BUILDING
FOR SOAP MANUFACTURE

FIG. 29

SEMIBOILED SOAPS

86. The term *semiboiled,* as applied to soap, refers to a soap that has not been grained, the saponification being completed in one change and the soap strengthened and settled in the following one. As the soap is not grained, in which process glycerine is separated, the kettle will contain, on the completion of the process, all the material that has been added to it. In semiboiled soap, rosin may be used as an ingredient, but the process is generally used only for straight glyceride stock.

87. As no impurities are removed in the waste lye formed by graining, it is necessary, in order to produce a superior quality of goods, that the stock used be of good grade. This process is often resorted to for the manufacture of the base for cheap toilet soaps. It is used generally for preparing the soap base for soap or washing powders, and is more quickly carried out than is the manufacture of settled soap. The stock can be killed (saponified) in the early forenoon, strengthened in the afternoon, and pumped to the crutcher, if a filled soap or a soap powder is to be made, or directly into the frame, if intended for toilet soap, on the following morning. If it is desired to save the glycerine and to remove the impurities as well, the soap may be grained sharply after the stock has been killed, the waste lye withdrawn on the following morning, and the soap carefully strengthened, settled, and pumped from the kettle on the third day.

88. The semiboiled process is primarily a cheap method of soap manufacture, with economy in fuel, labor, and time. The best plan, however, is to give the soap a simple purification by graining it sharply, thus prolonging the time consumed in manufacture by one day. If this is done, the grained soap should stand overnight before drawing the lye. By doing so, the volume and depth of color of the niger is greatly reduced.

The semiboiled process is used as well for the manufacture of soft soaps, of which textile soap is a variety, and for green

Castile soap made from olive-oil foots. A desired characteristic of the latter soap is the green color arising from the green coloring matter, or chlorophyl, present in the rind and pulp of the fresh olive. This soap is never grained. In graining, the coloring matter would be discharged into the waste lye, with the result that the finished soap would bleach rapidly and unequally on exposure, thus detracting from its appearance.

89. Manufacture of Soft Soap.—As the semiboiled process is used for the manufacture of soft soap, the boiling of this quality of soap will be discussed in outlining the practical features of the process.

Straight tallow or good grease stock, to which may be added some cottonseed oil, is run into the kettle on open steam. According to Table XIII, *Manufacture of Soap,* Part 1, for saponifying 10,000 pounds of tallow with caustic-soda lye of a density of 20° Baumé, made from 74 per cent. caustic, 9,795 pounds will be required. As tallow is a stock that is easily killed and gives well-defined indications of conditions in the kettle, practically all this lye may be added by the time the stock is in. Saponification, however, progresses in the meantime. The chief care is to avoid bunching, by boiling the contents of the kettle vigorously. Open steam is used throughout the process.

90. In the manufacture of settled rosin soap, a hard soap was produced; in the present case, however, it is desired to turn out a soft soap made with a soda base. According to an old definition, a soft soap is one in which the alkali used is potash. That definition is obsolete, for the hardness of a soap does not depend primarily on the nature of the alkali present, but on the degree of hydration of the soap. A hard soap can be made of potash and olein, which were the ingredients of the original Castile soap.

With settled hard soap, a yield of 150 per cent. is generally obtained; with soft soap, a yield may be obtained varying from 225 to 240 per cent. In fact, the yield may be any amount up to 400 per cent., according to the purpose for which the soap is intended.

desired. This arises from the greater combining weight of caustic potash, the molecular weight of caustic potash being 56, while that of caustic soda is 40; also from the fact that a potash soap in a hydrated condition will stand a greater amount of saline filling than will a soda soft soap.

Rosin is used to a great extent in soft soaps, but it should never be present in textile soaps. Linseed oil is extensively used in European practice, and, in fact, may be said to be the chief ingredient. Soft soaps admit of adulteration to a high degree, the principal cheapeners and adulterants being aqueous solutions of sodium silicate, soda ash, and potassium chloride; starch is also largely used.

95. Calculation of Yield.—To ascertain the net percentage of yield, simply divide the net weight of soap made by the weight of soap stock used. To arrive at the total yield, the numerator is increased by the weight of the filling material added to the soap in the crutcher or in the kettle.

COLD-PROCESS SOAP

96. In the discussion of the settled and semiboiled processes of soap manufacture, it was learned that the latter is the more economical, and for the manufacture of soaps of a certain character, it is the preferable one. The ease with which the soap can be purified by graining and removing the waste lye containing the impurities, indicates the looseness of the line of demarcation between the two processes. In the discussion of the manufacture of soap by the cold process, a method that surpasses all others in the economy of every element entering into the cost of production, is introduced. The method, however, possesses certain paramount disadvantages, which restrict its use to a very limited field, notwithstanding the large amount of soap of this character that is produced. The mechanical equipment required consists simply of tanks containing the fat, oil, and caustic-soda lye; a crutcher in which the ingredients are mixed; and frames to receive the mixture and in which, under favorable

conditions, the chemical reaction of saponification continues to completion.

With such simple and comparatively inexpensive factory equipment, it will be evident that the proportion of fixed charges in the cost of the product is very small. Experience is the chief and most important asset, without which, notwithstanding the simplicity of the process, satisfactory results cannot be assured.

97. The term *cold process* is loosely descriptive. The saponification is not conducted in the cold, for the heat generated by chemical combination is considerable. The term has reference chiefly to the fact that heat is not employed as in the two general processes previously described, only enough heat being used to insure the liquid condition of all the ingredients.

The theory of the process is very simple. The essential requirements are that the ingredients taking part in the reaction be intimately mixed. To effect this, the fat or oil must be in a liquid state and the caustic-alkali solutions must be maintained at such a temperature that when the stock and alkali are mixed, neither will cool the other to stiffness before every particle of the glyceride is brought into contact with the alkali. Even in the daily working of the process, it is a very difficult matter to maintain uniform conditions and to insure the complete absorption of the alkali. As the process is ordinarily practical, saponification is invariably incomplete, with more or less free fat and free alkali remaining in the finished product. This is the chief disadvantage of the process, and is the one that greatly restricts the use of cold-process soap for toilet purposes.

98. To secure satisfactory results in the practical working of the process, it is necessary that the caustic alkali be of high grade, not of lower quality than 76 per cent., and that the glyceride stock be fresh and pure. Without these primary qualifications, good results under no circumstances can be assured; but with them, the prime essentials of satisfactory work are obtained.

Coconut oil, either alone or in admixture with tallow and cottonseed oil, is chiefly used for cold-process soap. The rapid absorption of alkali at a comparatively low temperature, with the production of a smooth, clear soap that will neither crack nor warp on aging and that will admit the incorporation of a large amount of filling, make this oil especially adapted as a raw material for soap of this character. With inferior grades of coconut oil, boiling on strong caustic of 36° Baumé with open steam will remove what free fatty acids there are present, and these, with the impurities, will easily settle out. The same preliminary purification is also required for tallow.

The manufacture of cold-process soap received great impetus from the manufacture of high-grade caustic soda; the impurities always present in low-grade caustic interfered greatly with the satisfactory working of the process.

99. Manufacture of Cold-Process Soap.—To explain the process in practical detail, the manufacture of cold-process soap from 500 pounds of coconut oil will be discussed. By referring to Table XII, *Manufacture of Soap,* Part 1, it will be found that coconut oil will absorb about 17.6 per cent. of chemically pure caustic soda. This amount is equivalent to 18 per cent. of 76 per cent. commercial caustic; therefore, 90 pounds of caustic soda of this grade will be required for saponification.

A caustic-soda lye of 35° Baumé, made from 76 per cent. caustic, contains 28.28 per cent. of sodium hydroxide. Therefore, to furnish 90 pounds of sodium hydroxide, 318 pounds of 35° Baumé caustic lye, made from 76 per cent. caustic, will be required

100. The purified coconut oil at a temperature of 115° to 120° F. is run into the crutcher, and the latter is then agitated. The required amount of lye is then run in, and crutching is continued until a portion of the mass removed on a paddle appears clear and homogeneous. This condition can be ascertained only by experience, and under no consideration should the contents be removed from the crutcher until the most thorough mixing possible has been effected. The mixing

period need not exceed from 20 to 30 minutes, and with experience the time required is usually less. The mass is then dropped into frames, which are removed and carefully covered with soda-ash bags or other suitable material so as to prevent too rapid cooling. The frames should not be exposed to currents of cold air nor in any way subjected to rapid cooling.

101. There were added in the crutcher 500 pounds of coconut oil and 90 pounds of solid caustic dissolved in 228 pounds of water. This mixture yields a soap that, in so far as hydration is concerned, corresponds to the composition of unfilled settled soap. A yield of practically 63 per cent. has been obtained. By adding tallow and cottonseed oil in suitable proportions, the cost of the soap may be greatly reduced; also, the yield may be increased and the cost greatly reduced by the addition of sodium silicate, soda ash, pearl ash, mineral soap stock, starch, or talc.

102. All the filling material in cold-process soaps is generally mixed with the lye previous to being added in the crutcher. If it is desired to perfume the soap, the essential oil is added directly to the mass in the crutcher toward the end of the mixing process.

It should be borne in mind that the more highly filled a cold-process soap is, the more is the process of saponification retarded through the presence of inert material. Cold-process soap will admit of more filling than will settled soap without a corresponding deterioration of appearance on aging.

The substitution of caustic potash for a portion of the caustic soda is desirable, as a clearer, smoother, and milder soap will result.

103. In the procedure just described, there has been no interference on the part of the attendant. The ingredients were mixed in the calculated proportions, and the mixture thus obtained was treated mechanically in the hope that the results would be satisfactory. As experience in the operation of the process is acquired, the treatment may be modified

according to the judgment of the attendant. In the following procedure the judgment of the manufacturer is called into play.

Add the coconut oil at a temperature of 115° F. to the crutcher and start it slowly; then add gradually the caustic-soda lye, which was prepared at the same temperature. When all the caustic-soda lye has been added, continue crutching at the same or only slightly greater speed for a period of 5 minutes. At the expiration of this period, stop the crutcher and enclose it with a cover and soda-ash bags so as to retain the heat. Allow the mass to stand for an hour and then start the crutcher slowly. If a simple mixer

TABLE VI

FORMULAS USED IN MAKING COLD-PROCESS SOAP

Ingredients	Formula No. 1 Pounds	Formula No. 2 Pounds
Tallow	75	75
Coconut oil (Ceylon)	25	25
Caustic-soda lye (35½° Baumé) made from 75 per cent. caustic	75	70
Silicate of soda, N grade . .	125	100
Pearlash lye, 36° Baumé . .	20	17
Amount of soap produced . .	320	287

of style A, Fig. 6, is used, the contents should not rise above the level of the topmost horizontal arm; if it does, this portion of the contents will not be thoroughly mixed. With a crutcher of style B, Fig. 7, the contents should not rise above the level of the central cylinder enclosing the screw. With a steam-jacketed crutcher, the process can be more easily controlled through the use of steam, should the temperature fall below that ascertained by experience to be best, namely, 160° F. If at this stage the soap should show an excessive sharpness to the tongue, a few pounds of coconut oil may be added and crutched in until the soap tastes free

from caustic. On the contrary, should the soap, after the maximum heat of the reaction has been evolved, be neutral to the taste, a few pounds of 15° Baumé caustic-soda lye may be added and thoroughly incorporated. After these adverse symptoms have been corrected, start the crutcher at full speed and continue crutching for fully 20 minutes, until the mass rises white and smooth to the top of the crutcher. The perfume is now crutched in and the soap framed.

104. Manufacture of Cold-Process Soap Directly in the Soap Frame.—It is possible to make a fairly satisfactory cold-process soap directly in the soap frame, thereby eliminating the crutcher. Elkington has given instructions for the manufacture of cold-process soap by this method according to the formulas given in Table VI.

105. Weigh out the proportions of tallow and coconut oil required for a frame of soap into a tight frame. Weigh out the quantity of caustic-soda lye required into a separate vessel; also weigh out the proportion of silicate of soda needed into another vessel. The pearlash (crude potassium carbonate) solution is then weighed out and mixed with the silicate of soda. When all is ready for mixing, the temperature of the tallow and coconut oil in the frame should be from 145° to 150° F. in cold weather and from 125° to 130° F. in warm weather. The caustic-soda lye, and silicate of soda mixture should be at the normal temperature of the factory.

When the temperature conditions are as just stated, the caustic-soda lye is run alone and quickly into the frame containing the mixed tallow and coconut oil, the mass in the meantime being crutched vigorously from the bottom of the frame. After adding the caustic-soda lye, crutching should be continued until the mass begins to thicken. The mixture of sodium silicate and pearlash lye is now added quickly, with continued crutching.

106. After the last addition, the mass in the frame will be thinned out considerably and with continued crutching will gradually acquire a thick, creamy consistency. The two hand

crutches are now removed, and the frame is carefully covered and allowed to stand without disturbance until the soap is cold. If the soap is to be perfumed, the essential oil is stirred in with the silicate of soda mixture and added with it. If the frame must be moved from where the soap is made, move it quickly before the silicate of soda mixture is added; then add this mixture at once and finish the soap as directed. The cold process is primarily a quick process, the tardy addition of any ingredient being sufficient to mar the results.

107. For a 1,000-pound frame, the caustic-soda lye must be run into the soap stock in from 90 to 120 seconds. The addition of the silicate of soda mixture should also not require more time than this. Two crutches (see Fig. 15) should be used, the work carried on quickly, and the bottom of the frame reached at each stroke. With satisfactory conditions of temperature, the time required in preparing a frame of cold-process soap as just outlined should not exceed from 12 to 16 minutes. Care should be taken not to crutch the mass too long. To insure a smooth soap, crutching should be stopped as soon as a mark made on the surface of the soap will remain, and under no circumstances should the frame be disturbed until the contents is cold. With good, firm tallow, cottonseed oil may be substituted for it to the extent of 30 to 50 per cent., and less if the tallow is softer. With soft stock, more time will be required for cooling.

108. The apparatus used in cold-soap manufacture admits of very convenient arrangement. The soap-stock and alkali tanks should be placed on an elevation above the crutcher and should be provided with closed steam coils for heating the contents to the required temperatures.

Successful operation can only be carried out by weighing the stock and the alkali. If two scales are available, tanks sufficiently large to hold stock for five frames may be used, the weight each time being taken by difference. The stock and alkali are run from the storage tanks to the weighing tanks, and from there to the crutcher. If only one scale is available, the tank need be only large enough to charge one

frame, the stock being weighed out and emptied into the crutcher, and after this the alkali and filler, if any is used. In this manner, mistakes in the weights of the material used may be avoided.

109. In summing up the advantages and disadvantages of the cold process, it may be stated that the soap is simply, easily, and quickly made, with but little outlay for plant and labor. It admits of a greater yield than that furnished by any other process for the manufacture of hard soap. A well-made cold-process soap has not only a better appearance than a boiled soap, but retains its good appearance longer. It admits of a greater degree of filling than does a settled soap. The process differs greatly from the boiled processes in one important particular, namely, that small quantities can be made at a time. The process is used extensively for cheap toilet soaps, in few instances for laundry soap, and almost entirely in the manufacture of chipped soap that is sold to laundries.

As ordinarily practiced, the process does not admit of complete saponification, as do the boiled processes, the soap invariably containing, according to the care and experience used in its manufacture, greater or smaller amounts of free caustic alkali and uncombined fat or oil. Rancidity soon develops from the presence of uncombined oil. This is the chief, and practically the only, disadvantage of the cold process.

MANUFACTURE OF SOAP
(PART 3)

REMELTING OF SOAP

1. Purpose of Remelting.—Soap scraps result from various sources, which may be enumerated in the order of their occurrence, namely, frames of soap that have cracked or fissured or for any cause are not suitable, either in whole or in part, for slabbing and cutting; scrapings from frame bottoms; defective bars and trimmings from the cutting table; spoiled bars from the soap press; and unsatisfactory boxed soap returned by the trade. Such soap contains its proportion of the filling added in the crutcher, and if the soap were returned directly to the soap kettle, this filling would be lost in the waste lye. The function of the remelter is to remelt these scraps, and when melted, the soap is crutched and framed as before. Whenever possible, it is more economical to use up the clean scrap in the crutchers. The small amount that cannot be utilized in this manner may be boiled over again.

2. Some perfume and usually a small quantity of soda-ash solution are generally added to the remelted soap in the crutcher. The texture of remelted soap, when cut and pressed, differs from that of freshly pressed soap in being less clear.

When possible, it is always best to place the remelter above the crutchers and not to crutch the remelted soap alone, but to mix it with fresh soap coming from the kettle. The amount of soap, or scrap, to be remelted is usually equal to about 10 per cent. of the output of the factory, so that if

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

frames having a capacity of 1,200 pounds are used, each crutcher should have 120 pounds of remelted soap added to it. By following this method, a uniform product is possible—one feature of the soap trade that is very essential in order to insure a successful and profitable business.

3. Remelters.—As shown in Fig. 1, a remelter consists of a sheet-steel tank with a system of closed steam pipes *b* arranged vertically inside and also a system of closed

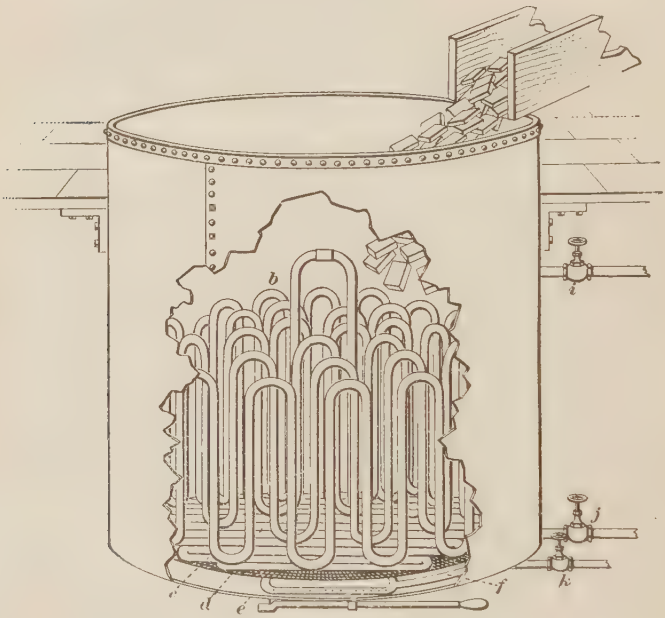


Fig. 1

steam pipes *c* arranged horizontally on the bottom and a short distance above the outlet *e*, the pipes *c* being connected with pipes *b*. A coarse wire netting *d* serves as a strainer; it is placed below the steam coils *c* and above the open steam jet *f*. The pipe *i* carries steam to the upright system *b*; the exhaust pipe *j* carries the water of condensation from the horizontal system *c*; and the live-steam pipe *k* supplies the steam jet *f*. The remelter is usually covered with insulat-

ing material, to retain the heat, and is surmounted by a wooden casing so as to receive the soap on the floor above. The steam pipes are so arranged as to distribute the heat uniformly throughout the mass and to interfere least with the flow of the melted soap, by gravity, from the bottom of the remelter.

4. When sufficient scrap for several frames has accumulated in the remelter, steam is admitted into the closed coils and the adjacent soap is melted. Live steam is then

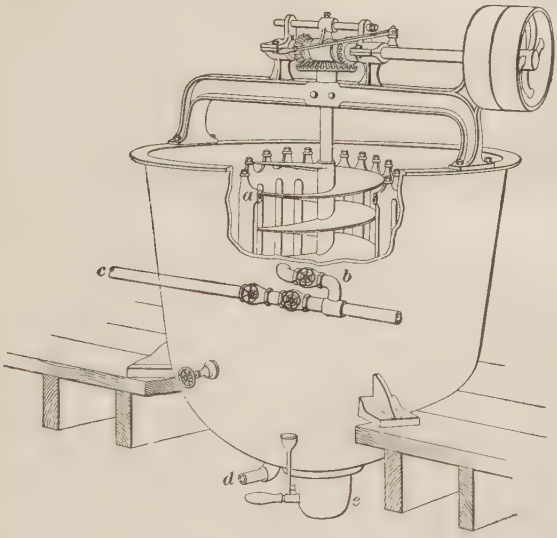


Fig. 2

introduced for a period of 10 minutes in addition to the closed steam. At the expiration of this period, the remelted soap should flow freely from the outlet. The live steam is now turned off. When a sufficient mass has melted to charge the crutcher, which is usually placed below the remelter in factories where a separate remelter is used, framing is begun and continued as fast as the soap melts. The remelted soap withdrawn is replaced by unmelted soap, which sinks by gravity from the wooden casing surmounting the remelting tank.

5. Remelting Crutcher.—When the size of the factory does not warrant the installation of a separate remelter, the latter may be combined with the crutcher, as shown in Fig. 2. The remelting crutcher, as this device is called, is a crutcher in which the inner concentric cylinder is replaced by vertical, closed steam pipes surrounding the screw. Steam is admitted into the vertical, closed steam pipes *a* through the valve *b*. Live steam is introduced at *c*, and the water of condensation is withdrawn from the closed steam pipes at *d*. The outlet of the crutcher is at *e*. The remelting of soap in this device is carried on practically the same as with the regular remelter. Soap scrap may be introduced by gravity from a receptacle placed above the crutcher.

MANUFACTURE OF TOILET SOAP

MILLED-PROCESS SOAP

6. The manufacture of toilet soap requires the installation of expensive machinery and a greater degree of skill than is necessary in the manufacture of laundry soap. Not only the cost of plant and the superior skill required in manufacture, but the experience and ability required in marketing the product, confine its manufacture to a comparatively limited number of plants. The manufacture of toilet soap in the United States dates from 1844, at which time a Frenchman, Jules Haul, made soap of this character with very primitive apparatus, in Philadelphia. Since the original manufacture of toilet soap in the United States, just noted, American skill and experience, together with the superior mechanical appliances employed, have so far advanced that the toilet soap produced in this country is equal to that produced elsewhere in the world.

7. Although toilet soap can be made by any of the three processes previously described, the term generally has reference to what is called a *milled soap*, meaning by this a soap

that, after having been partly dehydrated, is kneaded into films of dough-like consistency in a machine called a *mill*. The soap is then compressed into an elongated bar, which is cut into sections and pressed into separate cakes.

By this process of manufacture it is possible to combine the finest style and finish with superior quality and durability. Owing to the partial dehydration to which the toilet-soap base has been subjected, its milling, and the subsequent compression in the plodder, soap manufactured in this manner is the most economical for toilet purposes.

8. Toilet-Soap Base.—The manufacture of toilet soap requires first the manufacture of what is commonly called the *toilet-soap base*. This may be either a well-made settled soap, a semiboiled soap, or a cold-process soap. The principal requirements of a good toilet-soap base are that it be made from fresh material of good quality, be free from impurities, completely saponified, perfectly neutral, and of a good, tough grain. In large establishments, the manufacture of the toilet-soap base is usually entrusted to one man having special skill in the boiling of soap for this purpose. The nature of the stock used is very important.

Good, fresh tallow, with the characteristic shortness of grain of the soap made from it, softened by the addition of suitable proportions of cottonseed oil or a good grade of white grease, and smoothed with a proportion of coconut oil, will make a first-class toilet-soap base.

9. The formulas of the toilet-soap base vary greatly. Castor oil and lard may be used to make the soap milder and to admit of a finer finish in the pressed bar. In the manufacture of cheap toilet soap—what is known in the trade as five-and-ten-cent goods—not only is material of inferior quality used, but also adulterants well known to the toilet-soap miller. A fragrant and lasting perfume may also be added. Palm oil forms an excellent ingredient of the toilet-soap base, the natural odor of the oil harmonizing well with the perfuming material.

In the boiling of the toilet-soap base, the greatest care lies in completely saponifying the stock. In the use of coconut and cottonseed oils, this complete saponification is very important, for there are no oils used by the soap maker that are more liable to become rancid, especially when present as unsaponified stock in the finished soap, the rancidity being invariably betrayed by the odor on the hands after using.

10. Boiling Toilet-Soap Base.—The manufacture of the toilet-soap base does not differ essentially from the manufacture of settled rosin soap. Too much stress cannot be laid on the facts that the stock must be pure and fresh, the kettle and all appurtenances scrupulously clean, and that completeness of saponification must be insured. Covers for the kettles are usually provided in order to keep out dirt and to hold the heat for a longer settle.

The stock change is effected as previously described, care being taken to kill the stock thoroughly, even though the stock lye may contain an excess of caustic alkali. A slight strength is desirable, as it is believed that the texture of the soap is improved thereby. After graining and settling the waste lye, the latter is run off. The soap is then boiled, or strengthened, with the addition of weak caustic lye, after which it is grained sharply with undiluted caustic lye. This strength lye is withdrawn and held in storage for use in inferior grades of soap. The soap is now boiled up with live steam, and water is carefully added until the soap shows a characteristic flat grain and is all but closed. The soap is now allowed to settle, as on the settling change in the manufacture of settled rosin soap.

11. The success of a toilet-soap settle can be determined by comparing the amount of water in the soap at the time of finishing with that of a 2- or 3-day settle. When the steam is shut off, a sample will show 40 to 47 per cent. of water; if the settle shows 30 to 31 per cent. of water, it will make good soap. Much variation from these figures will result in an

unsatisfactory product when the soap is framed. It is believed that the more completely settled a toilet-soap base is, the better adapted it is for milling, due to the separation of salts and impurities that tend to form the niger. The more thoroughly these are removed, the less liable is the soap to come from the plodder in a cracked condition. At the expiration of the settling period, the soap, if no filler is added, is pumped directly into frames.

12. The nature of the process to be used in the preparation of the toilet-soap base and the care to be taken in the operation are determined by the quality of the product desired. For cheap, milled soaps, a base made by the cold process may be used, but more generally one made by the semiboiled process is used. With the latter process, the soap should be carefully settled; then the niger, if stock of good quality is used, can be incorporated in a succeeding boil or, preferably, added to a kettle charge for laundry soap. The soap is framed in the regular way and when cold is ready for cutting.

In the manufacture of hard soap, free from filling, whether by the settled, the semiboiled, or the cold process, the yield is commonly estimated as 50 per cent. This, therefore, gives the toilet-soap base, by whatever process it is manufactured, a water content varying from 30 to 33 per cent. To insure a satisfactory product on milling, this percentage of water must be reduced about 50 per cent. With settled soap for laundry purposes, the water content was reduced from 3 to 5 per cent., just sufficient to permit a good finish on pressing and stamping.

13. Preparation of the Toilet-Soap Base for Milling. In preparing the toilet-soap base for milling, the frame of soap is cut into long bars of such dimensions that the preliminary drying is effected in the quickest manner. At this stage it is merely desired to dry the soap, so that it can be reduced to chips in a cleanly manner. The superficially dried bars of soap are laid lengthwise in the feed-box *a* of the automatic chipper shown in Fig. 3, when they fall by gravity against the

knives set in the radial slits *b*, two of which are shown. The soap can be cut into chips of any desired thickness by adjusting the knives at varying distances above the surface of the disk *d*, which is rotated by a pulley on the shaft *c*. The chips are collected on the opposite side of the machine and spread on the bottoms of trays. These are then transferred to the drying room, where they are allowed to remain until the water content has been reduced to that degree permitting the most satisfactory treatment in the milling machine.

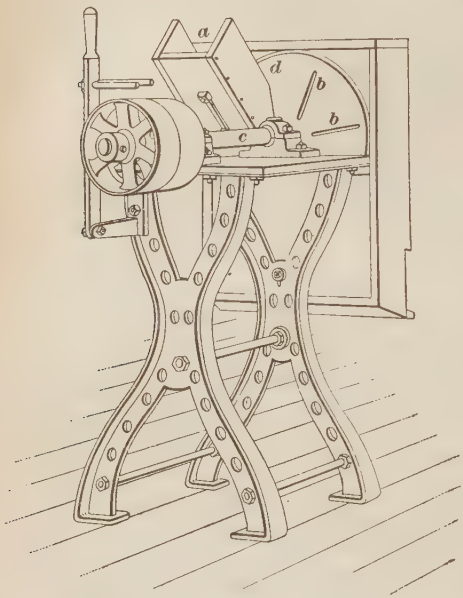


Fig. 3

14. A very convenient arrangement for the drying of toilet-soap chips is shown in Fig. 4. Air is forced over the soap contained in the trays of the case *a*, by means of the blower *b*, and escapes by means of the stack at one end. In the illustration the casing is partly broken away so as to show the location of the blower. The degree of dehydration is variable, depending on the quality of the product desired.

If cheapening material is to be added in the mill, its capacity for moisture demands that the chips be not too dry, or the soap will come from the plodder in a cracked condition. Again, with unfilled toilet soap, the consistency of the mass may be varied at will by suitable treatment during the milling process. If the soap works too dry in the mill, either softer soap of the same quality or some water may be added, according to the judgment of the miller.

The continuation of the drying process is best determined by experience. For goods of superior quality, the chips are sufficiently dry when the water content has been reduced from 30 or 33 per cent. to 15 or 18 per cent. The chips are now ready for the amalgamating and the milling processes.

15. Amalgamator.—The amalgamator consists essentially of a rectangular box, set on a frame, and equipped with a horizontal shaft through the center of which are set paddles, as in the horizontal crutcher. It has for its object the mixing of the perfume and color with the dried soap before milling, and by its use one or two millings are saved. By the old

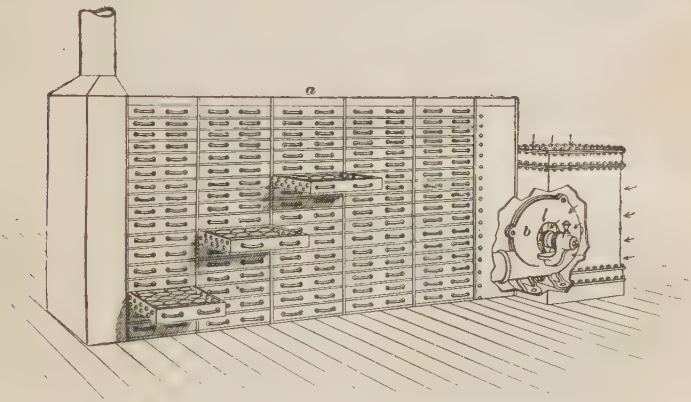


Fig. 4

method, the chips, color, and perfume were mixed in a box with a shovel. A very uniform mixture is possible with the amalgamator.

16. Toilet-Soap Mill.—The toilet-soap mill, shown in Fig. 5, consists of a hopper *a*, in which the soap to be milled is placed, set on rolls *b* and *c* of a series of granite rolls *b*, *c*, *d*, and *e*. These rolls vary from three to five in number. They are carried on heavy steel shafts, forming the core of the roll, and are mounted in the most improved machines one above the other at an angle of 45°. Granite, with a smooth and true finish, is generally used for the rolls, which

vary in diameter from 8 to 18 inches, and in length from 16 to 24 inches or longer, as desired. The capacity of the mill is rated by the manufacturer according to the amount of soap milled per hour, varying from 80 to 250 pounds for the roll dimensions just mentioned. The roll *c*, Fig. 5, is supported in stationary journals. The intervening distances between adjoining rolls may be varied at will by means of setscrews on both sides of the mill. In the illustration, the setscrews on one side are shown at *f*, *g*, and *h*. The rolls rotate on their shafts in the directions indicated by the arrows.

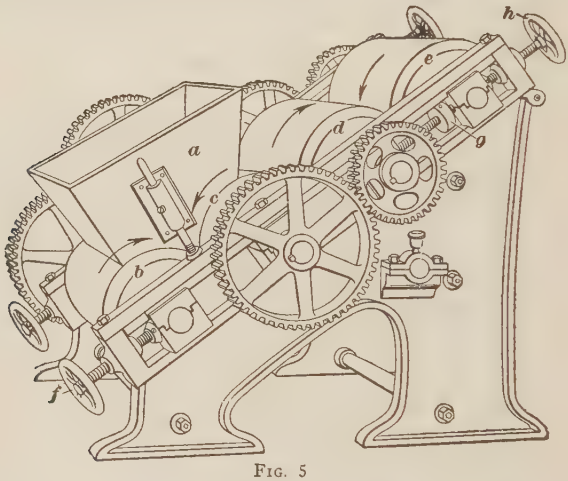


Fig. 5

17. Milling the Toilet-Soap Base.—When the chips are dried suitably and have the right **feel** when taken up by the handful, the amount required for a charge is introduced into the hopper and passed through the mill until reduced to a fairly homogeneous mass. One milling should suffice for this initial reduction.

During this preliminary milling, the distance between the rolls should be greater than at later stages in the milling process, owing to the coarseness of the material worked. During milling, the chips pass down between rolls *b* and *c*, Fig. 5, up between rolls *c* and *d*, and down between rolls *d* and *e*. Then,

in the condition of a thin, translucent film, they are removed by scrapers from the last roll and returned to the hopper, if desired, for another milling.

18. When an amalgamator is not used, and the proper consistency has been reached by milling, the soap is collected in a box, or trough, where the perfume and coloring matter in proportions based on the weight of the charge of soap delivered to the mill is added. If the perfume and coloring matter are in a dry state, it may be simply dusted on the soap in the mill. If liquid, they must be added to the shreds of soap resulting from the first milling and allowed to percolate through, yet not flow from, the mass. The soap is then transferred to the hopper and worked through the mill to the satisfaction of the attendant.

For cheap goods, three or four millings may suffice; for superior goods, or to produce the best possible texture in goods of any quality, seven or eight millings are required. After the milling process, the shreds of soap should be perfectly homogeneous, with the perfume and coloring matter, if any of the latter is used, thoroughly worked through.

19. Plodding Toilet Soap.—After satisfactory results have been obtained in the milling process, the soap is ready for the *plodder*. The soap as it comes from the mill is in thin, translucent laminæ. The function of the plodder is to compress this soap into a compact mass, which is expelled from the plodder in the form of an elongated bar. This bar is then cut into cakes of dimensions adapting them to the mold and die of the soap press.

20. Plodders.—The earliest form of plodder consisted of the naked hands, which molded the mass and crudely kneaded it with mortar and pestle into a globular or oblong bar.

The earliest form of machine plodder was a cylinder enclosing a screw, by means of which the soap that was fed into the cylinder at one end and above the screw was compressed. This is essentially the construction of the modern plodder. The improvements on this early form consist chiefly in

an increase and a more scientific distribution of the weight of the machine, and in the substitution of electricity as the source of power, thus permitting a greater compressive force to be applied to the soap. These mechanical improvements in the plodder have enabled toilet-soap manufacturers to produce a more compact, a more durable, and a better appearing piece of soap.

21. In the plodder shown in Fig. 6, *a* is the hopper into which the soap is placed; *b* is the case enclosing the horizontal

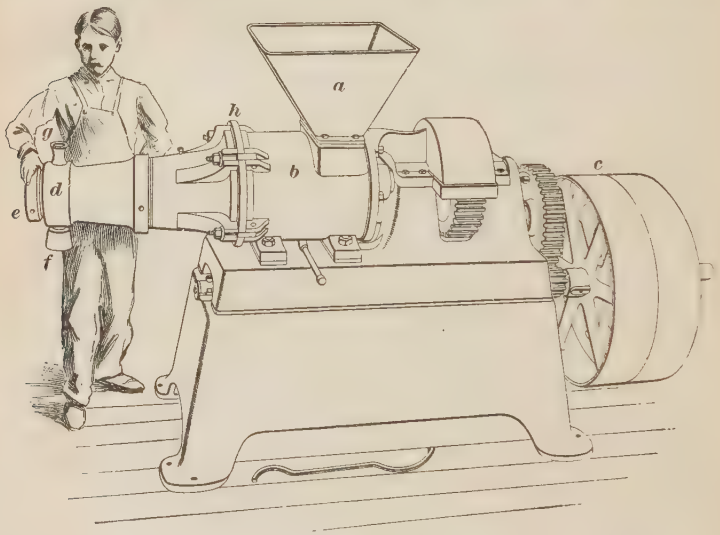


Fig. 6

screw compressor impelled by power applied by means of a belt to the pulley *c*; *d* is a concentric hollow casing enveloping the nozzle of the plodder, and is filled with water added at *g* and maintained at a definite temperature. The cake former *e* is heated by a gas flame applied at *f*, and it is screwed to the nozzle through which the elongated bar of compressed soap is forced. A sectional connection *h* of the screw case provides for the ready examination of the interior of the case. So long as soap is added to the hopper, the action of the plodder is continuous.

22. Plodders may be divided into two classes, according to the mode of applying the power, namely, the hydraulic and the motor-driven plodder. With the former, the output per day does not exceed 1,000 to 1,200 pounds of soap; with the latter, the output in the same length of time is much greater. The hydraulic plodder is being displaced by the motor-driven plodder, with its greater rapidity of operation.

The nozzle of the plodder is provided with a screw head, to permit the attachment of the cake former. With this arrangement the elongated bar is made to assume any

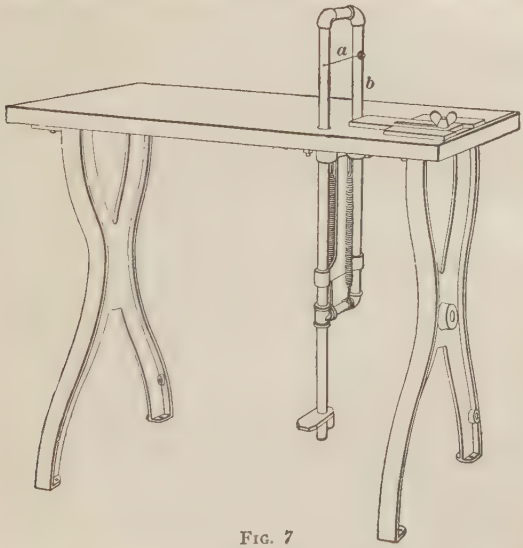


Fig. 7

cross-section desired, as circular, square, or rectangular. The purpose of the hot-water jacket, shown at *d*, Fig. 6, is to soften the soap to such a consistency that, when forced through the cake former, the cohesion of the soap mass will not be destroyed and the soap will not, as it is termed, "crack" or "splinter." Plodders are rated according to the pounds of soap capable of being plodded per day under a maximum average compressive force.

23. Cutting and Pressing the Plodded Toilet Soap. The soap as it is delivered from the nozzle of the plodder is

carried to the cutting table, shown in Fig. 7. Here, the long bar is cut into separate cakes of uniform length by the wire *a* in the movable frame *b* operated by foot-power. The experience of the attendant will determine at this stage whether it is necessary to subject the soap to a slight superficial drying in order to obtain the best possible impression on stamping. If the soap is sufficiently dry, it is taken from the cutting

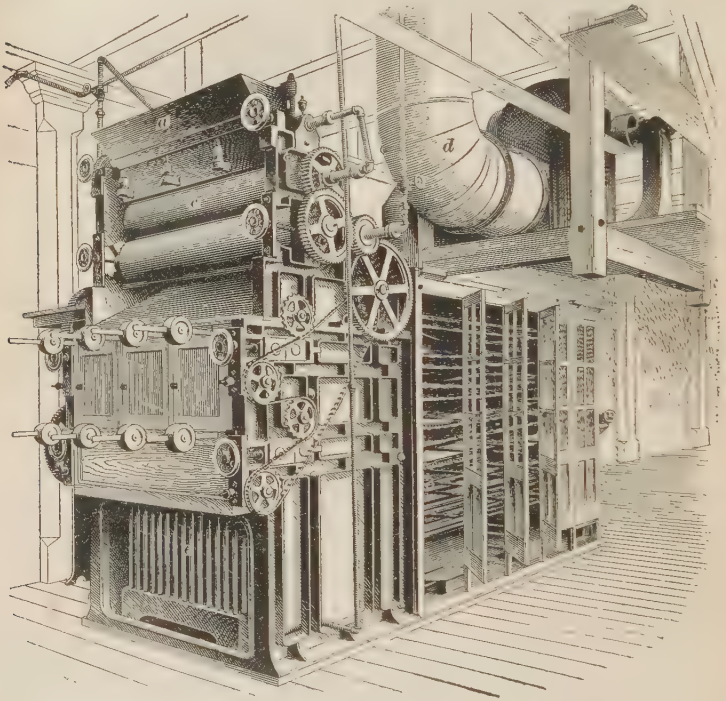


Fig. 8

table in trays to the soap press. Formerly all milled soap was pressed on old-style foot presses, but power presses have been improved to such an extent that they are now used in the larger plants. From the press, the cakes are taken to the benches for hand wrapping, or to automatic wrapping machines.

24. Continuous Crusher and Dryer.—The patented process known as the **continuous crusher and dryer**

possesses the double advantage of shortening the time of manufacture and of very materially decreasing the cost of production. In this process, instead of slowly cooling great masses of soap in bulk, the paste is treated while still hot and in a liquid state, just as it comes from the kettle. While available for household and industrial soaps, this process is used almost exclusively for toilet soaps.

In the manufacture of toilet soap by the usual process, as previously explained, the material is taken from the kettle, crushed, framed, slabbed, caked, and chipped before passing to the drying room. By this special process, however, the hot soap passes directly from the kettle to the machine in which the drying is to take place, the only intermediate step being the pumping of the soap from the soap vat to the storage tank. This is done in order to elevate the soap above the crusher and dryer and to regulate its flow into the hopper *a*, Figs. 8 and 9.

The mixing tank *b*, Fig. 9, is discarded by most users of the machine, the color and perfume being added to the dry and cold soap in the mixer *f*.

25. A boiled settled soap is usually crushed while at a temperature of from 65° C. to 70° C., but soap can be pumped to this machine at a temperature of 80° C. The soap paste passes from the hopper to the first roller *c*, Fig. 9, of the five horizontal rollers *c* to *c''''*. The speed and pressure of these rollers gradually increase in the order in which they are lettered, being greatest at roller *c''''*. The soap paste striking the rollers curdles at once and gets crushed into thin layers, which a knife divides into ribbons. The soap leaves the rollers *c''''* as a thin ribbon, or film, and falls on an endless band of wire gauze circulating in the drying chamber. These bands are shown through the open doors in the side of the apparatus, Fig. 8. The time required for the soap to pass from the hopper through the dryer to the box *d*, Fig. 9, is only about 12 minutes, during which period it travels the full length of the dryer a number of times, falling from one wire band to another.

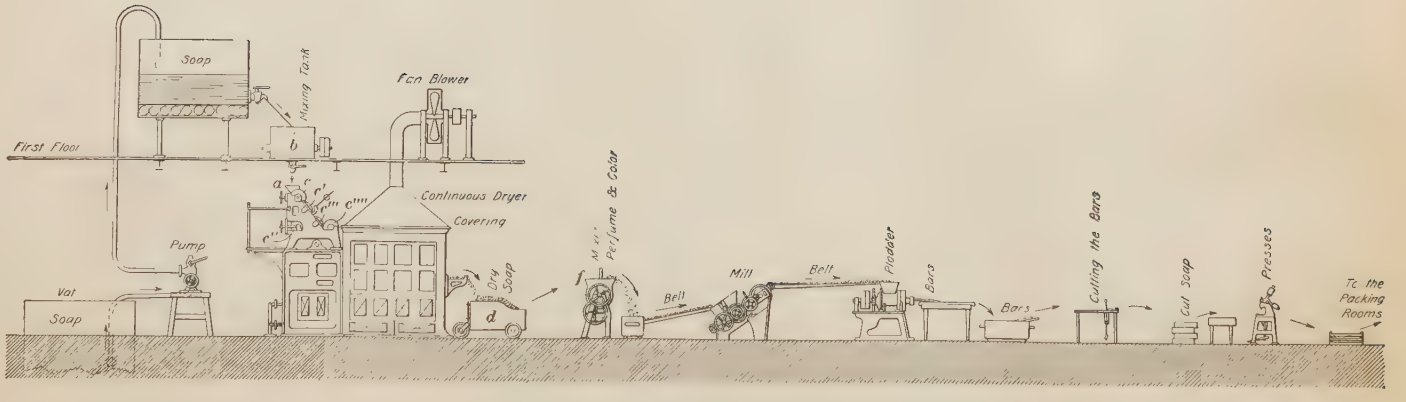

Soap
Mixing Tank
Fan Blower
First Floor
b
a
c
c'
c''
c'''
c''''
Continuous Dryer
Covering
Pump
Vat
Soap
Dry Soap
d
Mixer
Perfume & Color
Bell
Mill
Belt
Plodder
Bars
Bars
Cutting the Bars
Cut Soap
Presses
To the Packing Rooms

Fig. 9

The dryer is heated by the steam coil *e*, Fig. 8, and the hot and moist air passes away through the pipe *d*. The temperature maintained in the dryer is about 35° C., as this has been found to give the best results.

These machines are constructed in various sizes, and their output ranges from 250 to 800 pounds per hour.

PERFUMING OF SOAP

PURPOSE OF PERFUMING

26. Competition in the toilet-soap business has reduced the profit to a very small margin. One important characteristic of this business is the manner in which the goods are put on the market. An attractive wrapper and an agreeable perfume are demanded by the inexperienced buyer of this class of soap to the exclusion of the essential qualities. By means of coloring matter and suitably blended essential oils, a milled soap made from very inferior stock may have its original inferiority completely obscured.

27. The blending of essential oils is a recognized art, whose development requires the constant attention and study of the skilled perfumer. The demand is always for something new, to supply which the toilet-soap manufacturer is often hard pressed. Organic chemistry has supplied the perfumer with a large and increasing number of artificial perfumes, which often surpass the natural source in intensity of fragrance and cheapness. Some of these, as nitrobenzene, or oil of mirbane, a cheap and efficient substitute for the oil of bitter almonds for perfuming laundry soap, are obtained from coal tar; others, as vanillin, borneol, menthol, eugenol, ionone, heliotropin, etc., are prepared synthetically; certain others are isolated from essential oils, as safrol, from oil of camphor, which has practically displaced the natural oil of sassafras as a soap perfume; citral, from oil of lemon; carvol, from oil of caraway; etc.

PERFUMES USED IN LAUNDRY SOAPS

28. The following list of essential oils comprises those most commonly used for perfuming laundry soap. As has been noted, the proportion used seldom exceeds $2\frac{1}{2}$ pounds per frame of 1,200 pounds of soap.

Oil of caraway seed.

Oil of cassia, with guaranteed percentage of cinnamic aldehyde.

Oil of cedarwood.

Oil of citronella.

Oil of mirbane, artificial, with odor of oil of bitter almonds.

Oil of rosemary.

Safrol, artificial oil of sassafras.

Oil of eucalyptus

Oil of thyme.

29. The best way to ascertain the most satisfactory combination of essentials oils for a laundry-soap perfume is to prepare a number of mixtures to be used experimentally as a

TABLE I

FORMULAS FOR PERFUMING OF LAUNDRY SOAP

Essential Oils	Formula 1 Parts by Weights	Formula 2 Parts by Weights
Safrol	23	27
Cedarwood	12	10
Cassia	9	7
Lavender	10	10

basis, or vehicle, for a highly fragrant and strong-bodied essential oil, as artificial oil of sassafras, or safrol. This particular oil commends itself because of its cheapness. Its fragrance may be modified by mixing it in varying proportions with other essential oils, not debarred by their high cost, until a mixture is obtained that is at once cheap, lasting in fragrance, and disguises most completely and agreeably the odor associated with the soap in use.

After two or three mixtures of equal satisfaction are obtained experimentally, the mixtures may be subjected to practical tests by studying results when they are mixed in regulated proportions in successive frames of soap.

The formulas in Table I represent two mixtures, No. 2 being modified from No. 1 as the result of an advance in the price of cassia oil. Equally satisfactory results were obtained from both mixtures.

30. Laundry soap is seldom colored, indigo paste being the only color that is used to any great extent. The blue soap thus produced often misleads the consumer into the idea that bluing is being added at the same time that washing is being done. Unbleached palm oil is the cheapest and most efficient available agent to disguise the odor and color of rosin. Very small quantities of ultramarine are used in some cases to heighten the whiteness of floating soaps. Disinfectant and tar soaps are colored, the former variably, the latter with pine tar.

PERFUMING OF TOILET SOAP

31. The direct application of the perfuming material to the mass of thin, shredded soap, after its preliminary treatment in the mill to obtain homogeneity, involves no especial difficulty. A weighed or measured quantity of perfume is simply added to the mass in the box in which the shredded soap accumulates as received from the mill, and the perfume is then incorporated sufficiently with the soap to enable the attendant to transfer it to the hopper of the mill without waste.

The blending of perfuming material to obtain desired odors, generally those imitating the natural odors of fresh flowers, constitutes a distinct art and requires for proficiency an intimate knowledge of the chemistry of essential oils and experience in working with them. The various ingredients of the perfumed stock may be bought separately and then compounded or blended by the perfumer, or they may be bought already blended from dealers in essential oils and perfumers' materials.

32. With the exception of musk and civet, which are excretory secretions of the animals producing them, the raw materials of soap perfumery consist chiefly of essential oils obtained from wood, as oil of cedarwood; from bark, as the oil of wild cherry; from foliage, as oil of eucalyptus; from fruit or seed, as oil of caraway; and from flowers, the chief source, as oil of rosemary.

There is a large and increasing number of synthetic preparations and isolated bodies possessing in a marked degree the fragrance of the natural source that now successfully compete with the latter. These bodies, as a rule, are the odoriferous principle of the natural oil, and for purposes of perfumery are not encumbered with the non-essential ingredients present in the natural oil. A correspondingly smaller quantity can be used to effect the same results and thus generally reduce the cost of production.

33. The fractional distillation of essential oils obtained from plants has shown that they are composed of a nearly odorless vehicle, consisting of one or more hydrocarbons of the terpene class, a principal odorous constituent, which may be an alcohol, phenol, aldehyde, ketone, ether, or ester, and smaller quantities of various other compounds. These modifying constituents may vary in amount in oil obtained from different parts of the same plant.

COLORING OF TOILET SOAP

34. The operation of coloring is carried out in the amalgamator, in which the coloring matter, either dry or in solution, may be added to the soap. If an amalgamator is not used, the coloring matter may be added to the soap in the mill hopper or it may be spread out on the thin layer of soap as it passes on to the rolls of the mill. If it is deemed desirable, it may also be added directly to the soap in the box at the end of the mill after the soap has had a preliminary milling.

The application of the coloring material in solution is preferable to using material in the dry state, as it admits of a

more homogeneous distribution of the color in the shortest time. There should be a consistency between the nature of the coloring material used, the odor of the perfume, the character of the soap, and the name applied to it.

35. The organic coloring materials commonly used are obtained from coal tar and receive trade names that give no indication of their composition to the purchaser. Red, pink,

TABLE II

COLORS USED IN SOAP AND CHIEF MATERIALS FOR PRODUCING THEM

Color	Material
Red	Coal-tar colors: vermilion, Venetian red, alkanet, bole, colcothar, cinnabar, chrome red, carmine.
Orange and yellow	Coal-tar colors: chrome yellow, cadmium yellow, curcumin, gamboge, turmeric.
Green	Coal-tar colors: ultramarine green, chlorophyl extract.
Brown	Coal-tar colors: brown oxides of iron, mixed blue and yellow colors.
Blue and lilac	Coal-tar color: ultramarine blue.

orange, yellow, green, brown, blue, and lilac colors are obtained direct from the makers or already compounded from dealers in perfumers' materials and with guaranteed solubility in definite parts of hot or cold water. The primary qualifications of a soap dye are inertness to the action of alkali and permanency under the conditions in which the soap is used.

In Table II are given the chief materials used for producing various colors used in the coloring of toilet soap.

The intensity of the color is determined by the amount of dye used and the character of the soap. Coconut oil, for instance, as an ingredient of a toilet-soap base will permit of greater brilliancy than would be possible without its use.

MANUFACTURE OF SOAP POWDER

36. The manufacture of soap powder in recent years has grown into a business of considerable magnitude. The earliest of those engaged in its manufacture found the business extremely profitable, but with growing competition the margin has been considerably reduced. Well-made, settled, resinous soap can be filled with upwards of 10 per cent. of soda-ash solution with good results. If this filling is increased in quantity until present in the mixture greatly in excess of the soap, a compound results which, when reduced to a finely divided state, constitutes the soap or washing powder of trade. The first consideration in the manufacture of soap powder is the composition of the soap base. Any glyceride soap stock is available for this purpose. A good soap-powder soap can also be made by using corn or cottonseed oil and grease.

Rosin, which forms a soft, sticky soap, with great affinity for water, resulting in the formation of lumps in the powder, should not be used, or at best only in small proportion and in combination with a firm tallow base. The prime requisites of a soap powder are freedom from lumps, quick solubility, and uniformity of size of the particles composing it. Some soap powders are more finely divided than others, the degree of pulverization being determined by either the fancy of the manufacturer or the demand of the trade.

37. All soap powders are mixtures of soap, soda ash, and water, and vary only in the percentages of these ingredients and the kind of soap used in their preparation. They are divided into two classes, depending upon the amount of water present, and are called *old style* and *fluffy*. The old style contains 10 to 20 per cent. of water and the fluffy 30 to 40 per cent. Typical

analyses are given in Table III. With the old-style powder the lumps are coarse and harder because sufficient water is not present to form sal soda ($Na_2CO_3 \cdot 10H_2O$) with all of the soda ash (Na_2CO_3) present. For this reason considerable heat is felt when wet hands come in contact with it. This is its chief objection. The fluffy powder contains sufficient water to form sal soda with all of its soda ash and is soft to the touch. It occupies considerably more space than the old-style powder.

38. Manufacture of Old-Style Powder.—In the manufacture of old-style powder, the soda ash, soap, and hot water are dumped into a mixer of the horizontal crutcher type and mixed until the product is lumpy. A mixer charge is usually

TABLE III

ANALYSES OF SOAP POWDERS

	Old Style		Fluffy		
	1	2	3	4	5
Moisture	13.33	14.30	34.66	37.92	40.30
Dry soap	15.12	27.80	23.47	30.15	20.61
Sodium carbonate	71.55	57.90	41.87	31.93	39.09

based on the bag of soda ash, which weighs 300 pounds, as a unit. The lumpy material is then discharged from the mixer and raked through screens to break it up and to cool it as much as possible. It is then shoveled onto trays that have high sides. These trays are then piled up in a well-ventilated room. About 5 hours is required to set the powder under the best conditions. It is then ready for milling.

39. Manufacture of Fluffy Powder.—Fluffy soap powder is made by a continuous process. The material as it comes from the mixer falls upon a series of hollow rolls through which cold brine circulates. The rolls are arranged one above the other so that the thin layer of powder which is scraped from the upper roll, after it has made one revolution,

falls on the second roll, and so on until the powder is cold and crystallization is complete. The powder is then put through a screen, weighed, and packed.

40. Soap Base.—As a soap base, any settled or semiboiled non-resinous soap may be employed. If corn or cottonseed oil is used, the soap, after saponification, is grained with caustic-soda lye, which is later drawn to a kettle that is taking a stock change for a settled soap. The alkaline strength is then used up in saponifying part of this stock. If circumstances do not warrant the separation of glycerine by graining the soap, a semiboiled soap composed of simple ingredients will satisfy every requirement.

41. Soap-Powder Mill.—The soap-powder mill is of especial importance in the manufacture of soap powder, and

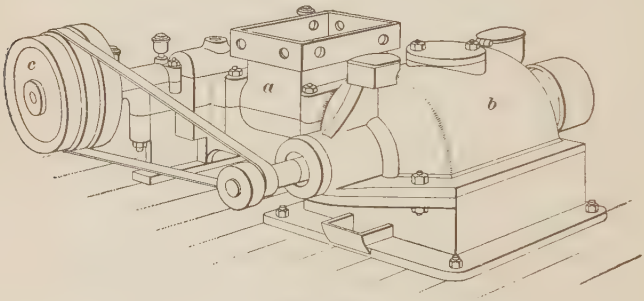


Fig. 10

should be so constructed as to do the work quickly, without heating the powder, and with a minimum of dust and repairs. The machine shown in Fig. 10 receives the trays of coarse soap powder, previously broken into lumps, in a hopper attached to the collar *a*, and crushes, grinds, and sifts it in one continuous automatic operation. The lumps are reduced by repeated blows of rapidly revolving steel blades, or beaters, enclosed in the semicylindrical casing shown at *b*. The powder is discharged through a semicylindrical screen, which serves as a sifter and which forms the under side of the casing *b*. Power is applied by belt at *c*. The mill is mounted on a well-braced framework that is completely enclosed to retain

dust and high enough to admit the introduction of a barrel to receive the powdered material. A newer style of mill employs the same principle on a larger scale, but is equipped with much greater screening surface.

42. The soap-powder department is usually arranged so that the mixers are on one floor, the mills on the floor below, and the weighing, filling, and sealing machines on the next floor below the mills. The weighing, filling, and sealing are all done automatically on special machines of which there are several types. The operations connected with soap powder making are very disagreeable because of the dust. All machines should be provided with hoods that have very strong exhausts.

43. Scouring Powder.—Scouring powder is also a soap-factory product. It is a mixture of soap powder, grit, and talc, with, at times, sal ammoniac. It requires no milling as all the ingredients are purchased in the powdered state. These are mixed, delivered by the conveyer to the weighing machines, filled and sealed into the cans or cartons. The various brands on the market differ in the amounts of their ingredients and in the kind of grit used.

RECOVERY OF GLYCERINE FROM WASTE-SOAP LYE

MANUFACTURE OF GLYCERINE

44. Historical.—Scheele, in 1779, when preparing lead plaster by heating olive oil with litharge, obtained a soluble, sweet-tasting substance, and later, in 1784, he found that the same substance could be obtained from other oils, as well as from butter and lard. To this material he gave the name *the sweet principle of fats*, and it afterwards bore the name of Scheele's sweet principle, or oil sugar.

Lead plaster is said to have been discovered by the Roman physician Menecrates about the middle of the 1st century, and also to have been known to Pliny, who briefly described

its uses, mode of preparation, and application, but nothing was known of glycerine until Scheele's day.

Later, the body was more carefully investigated by Chevreul, who determined its composition with tolerable exactitude and gave to it the name that it now bears. Pilouze in 1836 first established its formula. His experimental results corroborated Chevreul's views that the fats are ether-like compounds of the fatty acids. Henceforth glycerine became the subject of study by Berzelius, Liebig, Berthelot, and de Luca; but it remained for Wurtz to determine its exact chemical composition and relation to other bodies of the aliphatic series.

45. Scheele published the results of his investigations in a communication that appeared in the Transactions of the Royal Academy of Sweden, in 1783. He describes his method of preparation in the following terms: "It is not generally known that all solid oils obtained by pressure contain a natural sweet principle which differs in its special relations and properties from the other well-known saccharine materials occurring in the vegetable kingdom. This sweet principle makes its appearance when oils of this kind are boiled with litharge and water until the whole of the litharge is dissolved by the oil. Water is then poured upon the *emplastrum simplex* thus formed, the whole boiled for a few minutes, and on cooling the liquid is filtered off from the plaster and boiled until the residue becomes sirupy."

46. Glycerine was prepared by the foregoing process alone for many years, the lead introduced as an impurity from the litharge being removed, before concentrating the filtrate, by the use of hydrogen sulphide. This concentrated filtrate, after some primitive clarification, constituted the glycerine of commerce. Its rapidly increasing use soon demanded its production on a larger scale. It was known that in the process of soap making the glycerine liberated from the fat in the act of saponification remained in the waste lye, but efforts to recover it from this medium with the extremely crude methods used were unsuccessful.

In the meantime the manufacture of stearin candles was undergoing important developments. Numerous patents were granted for processes for the decomposition of the fats and the separation of glycerine. Gay-Lussac and Chevreul, in 1825, were the first to obtain patents. Their patent was for the alkaline saponification process, which, however, did not admit of successful operation until after the improvement by de Milly, in 1831. This is the *autoclave process* at present in use.

47. During the succeeding 20 years the sulphuric-acid distillation process was proposed and developed. Although other investigators had worked with the problem, and in fact a form of the process was in actual use, it remained for an American chemist, R. A. Tilghman, to determine the conditions productive of the most successful results. For his originality he received a patent in 1854. An English patent was soon after taken out. Tilghman's process is the one at present employed in conjunction with the use of sulphuric acid.

48. In 1847, Sobrero, in Paris, discovered nitroglycerine. Alfred Nobel demonstrated its value as an explosive in 1863 and in 1866 invented dynamite. This was followed in 1875 by blasting gelatin. The construction of vast engineering undertakings was greatly facilitated by the use of these substances, of which glycerine is the basis. The increased use of glycerine reacted directly on the source of the raw material, and the soap trade soon came to a perplexing realization of the increasing value of the product that was being daily consigned to the sewer.

49. Treatment of Waste Lye.—In the discussion of the manufacture of settled resinous soap, the progress of a boil of soap was traced, showing the formation of the various lyes. These are dilute solutions of varying percentages of sodium hydroxide, sodium carbonate, sodium sulphate, sodium chloride, and glycerine, and are contaminated by more or less soap in suspension, together with coloring matter intro-

duced by the rosin and with some mucilaginous matter or animal tissue remaining in the stock when rendered. This liquor, which often has a foul odor and is a by-product with the soap maker, now becomes the raw material of the glycerine refiner.

50. The process and apparatus used represent the culmination, in efficiency and simplicity, of all systems of glycerine recovery from waste lye. It has been declared impossible to prepare a chemically pure glycerine from waste lye—that glycerine of dynamite grade represents the limit in purity of glycerine obtained from this source. Soap lye, by the improved treatment at present in use, is made to yield a glycerine of the highest purity and answering the severest requirement of any pharmacopoeia. In the processes that have received the substantial approval of general practical use, the agents employed for the precipitation of albuminous and soapy matter and the neutralization of the alkali present in the lye are sulphuric acid, hydrochloric acid, alum, and a basic sulphate of iron.

51. The basic sulphate of iron is prepared by treating pulverized iron ore with sulphuric acid, whereby an acid salt mixed with some uncombined ore and acid is obtained. This mixture is subsequently subjected to a high temperature, namely, 380° to 500° F., when it undergoes a transformation into a basic sulphate of iron. The efficiency of basic sulphate of iron as a clarifying agent depends on the formation of ferric hydrate and insoluble iron soaps that entangle completely the albuminous matters, all of which in settling through the liquor clarify and decolorize it.

52. The waste lyes from the stock and wash changes are run into storage tanks situated in a convenient place below the soap kettles and above the treatment tanks so as to save pumping. Before they can be evaporated, the alkali must be neutralized to prevent frothing when boiled. The treatment also removes the mucilage and tissue. There are two general methods, one of which is a patented process that uses the

basic sulphate of iron previously described. The other one neutralizes about three-quarters of the alkalinity with hydrochloric acid, and the remainder with alum. The precipitated iron hydroxide in the first method and the aluminum hydroxide in the second do the coagulating and clarifying. In any treatment used, the lye is left after treatment very slightly alkaline, usually about .02 per cent.

53. Basic Sulphate-of-Iron Method.—The waste lye is run into the treatment tank and stirred with compressed air. A sample is taken and its alkalinity determined. The amount of basic sulphate of iron needed is dumped into the tank and the air turned on to keep it well agitated. In 20 minutes a sample is taken, filtered, and the alkalinity again determined. When the alkalinity is correct, the tank is emptied by pumping through a filter press into another storage tank from which the evaporators are fed.

54. Hydrochloric Acid and Alum Treatment.—The procedure is the same as that just described, except that three-quarters of the alkalinity is neutralized with hydrochloric acid and the remainder with alum. The operators in the glycerine plant are given tables by which the amounts of these chemicals needed for the alkali content are read off directly.

The entire glycerine recovery is controlled by a few simple chemical tests and the solutions and apparatus needed are placed in the glycerine-plant office. The use of these is taught to the men operating the treatment tanks, evaporators, and stills, so that the routine control work is taken out of the main laboratory, which is then concerned only with the more difficult work of testing the finished glycerine.

55. Evaporation of Treated Lye.—The next step is to remove the water and salt and concentrate the glycerine into what is known as *crude*. The crude contains from 77 to 85 per cent. of glycerine. This is done in an evaporator especially designed for the work. The evaporators are built in single or multiple effects. By multiple effects is meant, that the steam chest of the second effect receives its steam from the vapor

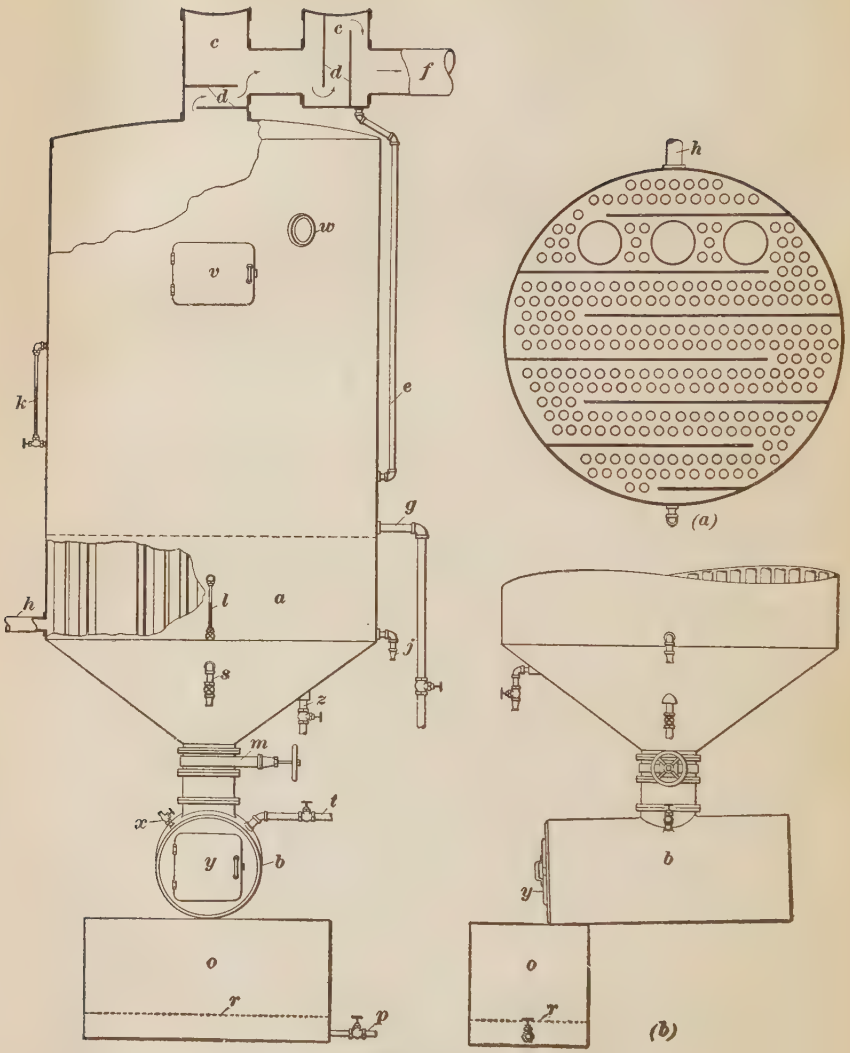


FIG. 11

line of the first effect. These evaporators are operated under a high vacuum, say 27 to 28 inches.

The evaporator shown in Fig. 11 is of the single-effect type. The process is the same with any number of effects, and for descriptive purposes the single effect is less confusing. It is a large tank built of steel plates. A steam chest *a* consisting of numerous small tubes to allow the circulation of the boiling liquor, and two or three larger tubes to increase this circulation, is built into the lower part of the evaporator. This arrangement also allows the salt, which is thrown out of solution as the concentration increases, an easy means of passing down into the salt drum *b*. The small drums *c* are placed at the top of the evaporator and fitted with baffles *d* to catch any entrained liquor and to return it by the line *e* to the evaporator. The vapors are removed by the line *f*, which is also connected with the pump which maintains the vacuum.

56. The treated lye is fed into the evaporator through the line *g*, Fig. 11. The steam chest is supplied with steam through the line *h*. For all light liquors, the boiling is done with exhaust steam, and, as it gets heavier, live steam must be used. The condensation is removed by the drip *j*. The height of the lye in the evaporator is controlled by the sight glass *k*, which is usually fitted with two bands to mark the upper and lower levels to be carried. The condensation in the steam chest is noted by the sight glass *l*, while *w* is a plate-glass window through which the boiling can be observed.

The bottom of the evaporator is fitted with a flange on which a large valve *m* is bolted, and below this valve is hung the salt drum *b*. A tank *o* is placed under the salt drum to catch and dry the recovered salt. This tank has a false bottom *r* which is connected with a pump *p* for drawing off as much lye as possible from the salt. The salt drum is provided with a vacuum line *t*. At some convenient place on the lower part of the evaporator handy for operation, a draw-off connection *s* is fitted for sampling. Fig. 11 (*a*) is a plan view of the top and bottom tube sheets of the steam chest, and (*b*) is a side elevation of the evaporator, showing the pitch of the salt

drum. The entire evaporator and lines are heavily insulated to conserve the heat.

57. Operation of Evaporators.—All the valves of the evaporator, Fig. 11, are closed except *j* and *m*, and that on the line *f*. A vacuum of 27 to 28 inches, or the capacity of the pump, is drawn and maintained. The valve on the line *g* is opened and lye drawn to the upper mark on the glass *k*. Steam is turned into the steam chest and the boiling continued with fresh additions of the lye as it boils down. With soap lyes containing between 3 and 4 per cent. of glycerine and varying amounts of salt, not much change is noticed for a few hours, but as the concentration of glycerine progresses, the salt is precipitated and in settling forces the lye out of the salt drum *b*. When the evaporation has continued for several hours, the valve *m* is closed, the vent *x* opened slowly to break the vacuum, and the door *y* is opened to drop the salt into the tank *o*. Some of the salt will run out, but most of it must be removed with a hoe. The boiling is not interrupted. The door facings are washed with water to make a perfect joint; this door *y* and the vent *x* are closed. A vacuum is drawn on the salt drum *b* through the pipe *t*, and when the vacuum of the drum equals that of the evaporator, the salt valve *m* is opened slowly, and the boiling-down process continued. This may be finished as a crude of 75 to 85 per cent. of glycerine, which is discharged to tanks through the pipe *z*. This crude has a specific gravity of about 33° Bé.

It is here that practice varies. The evaporators are usually made up of several units and are put on a schedule of *salt drops* and *lye drops* that are staggered in time, so as to keep the work continuous. The evaporation is carried to a *half crude* as one step and finished to crude as the second.

Smaller evaporators are used for the second step. Table IV shows to what extent the glycerine content of the liquor is increased, and the salt and sodium sulphate content is decreased, by evaporation.

To save as much heavy lye as possible and also to facilitate handling back to the soap kettles, the salt is made very dry

by the pump on the line *p*. At some factories the drying is done in centrifugals. Thus far the main object has been to

TABLE IV

EVAPORATOR LIQUORS

Degrees Baumé	Glycerine Per Cent.	Salt Per Cent.	Sodium Sulphate Per Cent.	Boiling Point Degrees C.
27.9	19.00	19.73	3.51	109
27.8	23.44	18.86	2.33	109
28.0	29.44	17.34	1.78	112
28.3	35.21	16.29	1.29	111
28.7	43.68	14.32	.82	113
29.5	56.17	12.52	.80	116.
33.4	81.90	6.82	.51	162
33.8	81.75	7.08	.22	167

remove, as far as possible, all water and salt from the lye and concentrate the glycerine in the crude.

TREATMENT OF CRUDE GLYCERINE

58. Crude Glycerine.—Crude glycerine contains from 75 to 85 per cent. of glycerol, about 6 per cent. of salts, chiefly sodium chloride, about 5 per cent. of organic matter, constituting the *foots* obtained on subsequent distillation, while the remainder is water. It is a thick, viscous liquid, its color and clearness depending in a great measure on the character of the stock and the efficiency of the preliminary treatment that the fresh lyes have received for the removal of organic matter, including iron salts of the organic acids.

59. Distillation of Crude Glycerine.—The crude glycerine is withdrawn into storage tanks, from which it is transferred, as required, to another vacuum apparatus in which the dillation is conducted. This apparatus comprises a large cylindrical sheet-iron tank, in which the crude glyc-

erine is distilled, and a series of vertical pipes terminating at the bottoms in horizontal cylindrical reservoirs, in which the distillate condensed in the vertical pipes collects. These reservoirs are termed *catch-alls*. A still 3 feet 6 inches in diameter and 6 feet high will have about seven catch-alls which may vary from 18 inches near the still, to 30 inches in diameter at the end of the system, all being about 5 feet 6 inches long. These catch-alls are in reality air condensers.

60. At the end of the series of catch-alls are two larger horizontal cylindrical vessels surmounted by an iron cylinder filled with water-cooled tubes, through which the more volatile portion of the distillate passes and is condensed, falling into the reservoirs below. These vessels, called *sweet-water drums*, communicate with a dry-air vacuum pump, which maintains a vacuum of about 28.5 inches throughout the system. Steam at a pressure of 125 pounds, corresponding to a temperature of 345° F., circulates in a closed coil and maintains a constant temperature.

61. Advantage of System.—The essential advantage of this system of glycerine distillation consists in the injection of expanded and reheated steam into the body of crude glycerine maintained at a high temperature. Glycerine has a boiling point of 290° C., or 554° F. Under atmospheric pressure, however, it cannot be heated to this temperature without undergoing decomposition. By reducing the pressure, as is done in a closed vessel when a vacuum is maintained, it boils without decomposition, and its vapor may be condensed unchanged. Commercial crude glycerine is very impure, the organic matter present causing difficulty in the refining process. To separate this organic matter effectually, recourse must be had to some means other than boiling at a lower temperature under reduced pressure. To accomplish this, a jet of expanded and reheated steam is introduced into the mass of crude glycerine heated to the temperature of distillation.

62. If steam at boiler pressure, namely, 125 pounds, were used directly for distillation without being previously expanded

and reheated, its expansion in the distilling apparatus would not only greatly retard, but would practically stop, the operation. To the great loss in heat due to absorption by the expanded steam would be added the difficulty arising from its condensation. These adverse and prohibitory conditions are eliminated by the use of expanded and reheated steam, which is prepared in the following manner: Steam taken directly from the boilers is allowed to expand in a coiled pipe of larger diameter located inside of a well-insulated vessel, called a *reheater*, which is attached to each still and in many cases is larger than the still itself.

63. The steam in expanding suffers a reduction in temperature. The heat lost is restored by surrounding the coil within the reheater with the same unexpanded steam from the boiler. Steam thus treated is introduced directly into the crude glycerine, which distils without decomposition at a temperature of about 300° F. Before introducing the steam, crude glycerine is added in sufficient quantity to cover the jet pipe to a satisfactory height, as indicated by the gauge glass, and as the distillation continues, crude glycerine is added from time to time in quantities not too great to interfere with the even working of the still, never, however, allowing it to fall below the established level. If, from lack of attention on the part of the attendant, an excessive quantity is introduced, there is great danger of the entrainment of the impurities contained in the crude glycerine, which increase in quantity in the still as the distillation proceeds.

64. Crude-Glycerine Still.—In the still shown in Fig. 12, A is the still proper, B the reheater, C and C' the catch-all drums, and D the sweet-water drum. In the still A, the closed coil, shown in dotted lines, carries steam at boiler pressure, which heats the contents of the still to the temperature required for distillation. In the reheater B, steam at a pressure of 125 pounds enters through the pipe a and expands into the coil of larger diameter, which is shown in dotted lines. This expansion coil is surrounded by steam at boiler pressure entering the reheater through the pipe b, which also carries

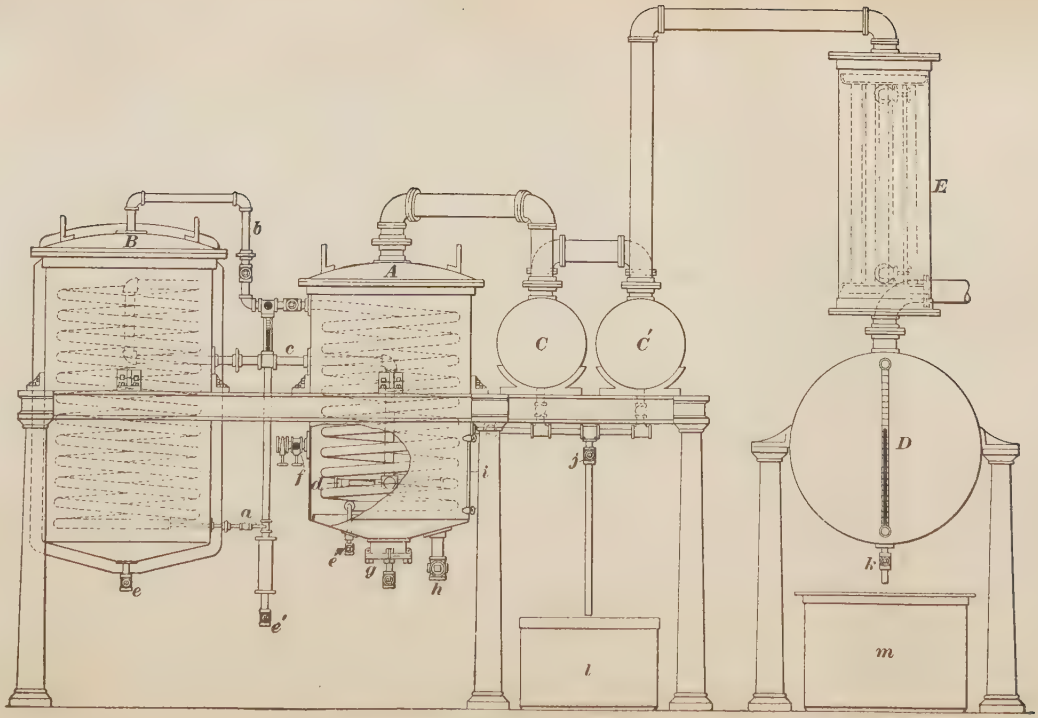


Fig. 12

steam at the same pressure into the heating coil of the still *A*. Expanded and reheated steam from the reheater enters the still through the pipe *c* and discharges into the crude glycerine contained therein through the crisscross jet shown at *d*. The catch-all stuff, so called, collects in the catch-all drums *C* and *C′*, and the lighter portion of the distillate condensed in the water-cooled jacket at *E* collects in the sweet-water drum *D*. At *e*, *e′*, and *e″* are outlets for the water of condensation from, respectively, the reheater *B*, the high-pressure steam line from the boiler, and the heating coil of the still *A*. At *f*, crude glycerine is fed into the still by suction. At *g* is the drop door through which the foots in the still *A* is discharged. Water used for washing the still is discharged at *h*. The level of the contents of the still is shown by the gauge glass *i*. At *j* and *k* are the discharge valves for the contents, respectively, of the catch-all drums *C* and *C′* and the sweet-water drum *D*. Tanks *l* and *m* are reservoirs for these respective portions of the distillate. All steam pipes leading to and from the apparatus, as well as the still and reheater, are insulated so as to retain the heat.

Before beginning a distillation, it is customary to have in stock a considerable quantity of crude glycerine, so that there will arise no necessity of shutting down the apparatus before conditions in the still render it imperative. Fresh lye is undergoing concentration all the time, and naturally the product of one operation comes in greatly reduced bulk to be the raw material of the next.

65. Tests During Distillation.—One of the chemical requirements of a dynamite glycerine is that it should not contain over .01 per cent. of salt. The best indication that a still has *boiled over*, that is, that some of the crude has been mechanically carried over to the catch-alls, is the presence of a high chlorine content in the distillate. It is possible to ascertain the amount of chlorine and control this part of the operation by providing the attendant with a simple chemical test and teaching him its use. All the catch-alls are fitted with sampling pipes. A large sample, say 50 to 100 cubic

centimeters, is obtained, a few drops of potassium-chromate solution added, the mixture diluted with distilled water, and titrated with a standard solution of silver nitrate, drop by drop, until the permanent silver chromate precipitate is formed. This silver-nitrate solution is of such strength that either 10 or 20 drops indicate the limit of salt allowed. The test is most valuable. The distillation runs a long time before dropping, say 24 to 36 hours, and it is very essential that the purity of the distillate should be known at all times. The controlling test

TABLE V

GLYCERINE DISTILLATES

Catch-All	Specific Gravity at 15.5° C.	Chlorine Per Cent.
First	1.2595	.0011
Second	1.2587	.0011
Third	1.2580	.0011
Fourth	1.2578	.0011
Fifth	1.2557	.0011
Sixth	1.2553	.0011
Seventh	1.2519	.0006
Eighth	1.2515	.0006
Ninth	1.2469	.0006
Tenth	1.2452	.0006

is made on the first catch-all, as it is nearest the source of salt. If it is very high in salt, the other catch-alls are tested, and if they all show high, the operation is stopped, the entire still and catch-alls washed out and the distillation started anew. If the first catch-all is only slightly over the limit, the distillation proceeds, as the other catch-alls will average the salt down. Table V shows the results obtained from an actual run of a 6-foot still fitted with ten catch-alls.

66. Products of Distillation.—The products of the distillation of crude glycerine may be separated into three

classes, namely, material collected in the catch-alls, technically called *distillate;* material of a much lighter gravity, called *sweet water*, consisting chiefly of water containing from no glycerine at all to as high as 12 per cent.; and a black, viscous residuum left in the still, constituting the *foots*.

67. Refined Glycerine.—The contents of the catch-alls still contain too much water and are removed to a cylindrical tank, called a *concentrator*, for further refining, which consists in the removal of water. The concentrator is provided with closed steam coils and a vacuum system. The distillate is transferred as quickly as possible from the still to the concentrator to save the heat, and the concentration is then continued. Practice dictates its length, but 2 to 3 hours is usually enough. At the end of the concentration some bone black, which acts as a decolorizer, is mixed with some of the distillate and drawn into the concentrator. The glycerine is then pumped through a small filter press that discharges directly into a covered tank. It is drummed at once from this tank, allowed to stand overnight to cool, and the drums filled up the next day.

Glycerine in any concentrated form must be handled very hot. Added to the slowing up in flowing when cold, is the danger of breaking the filter plates when cold glycerine is forced through them.

68. Sweet Water.—The material known as sweet water is concentrated to the consistency of crude glycerine and is then distilled and the distillate concentrated, as explained for refined glycerine. Another use is to take it back into an evaporator that is sluggish in its boiling to dissolve the salt that collects on the tubes of the steam chest. It saves the use of water for this purpose.

69. Foots.—There remains to be considered the black residuum, or foots, in the crude-glycerine still. All the organic matter not removed in the preliminary treatment of the lye accumulates in the still and forms this black, viscous residue, which, if the distillation is carried too far, becomes so hard that it is removed from the still only with great diffi-

culty. To facilitate its easy handling and the recovery of the large quantity of glycerine retained by it, the distillation is checked at that stage beyond which there is danger of contaminating the distillate with entrained matter from the still. The quantity of glycerine present in the foots depends on the concentration, and is about 50 per cent.

In the distillation of crude glycerine, the organic compounds of sodium do not precipitate as do the inorganic compounds, namely, sodium sulphate and sodium chloride, and the former, as the mass in the still undergoes concentration, remain to constitute the foots. There are present, usually, about 5 per cent. of salt, from 20 to 30 per cent. of sodium acetate, and from 10 to 15 per cent. of sodium salts of non-volatile organic acids.

70. While still soft and comparatively fluid, the foots are transferred to a tank and neutralized with sulphuric acid. After the gradual addition of the diluted acid and filtering, the product is concentrated, forming crude glycerine from foots; this is then distilled. About 1,200 pounds of foots is obtained from every 10,000 pounds of crude glycerine, yielding on distillation about 50 per cent. of glycerine.

It is the practice in some refineries to shut off the feed supply of crude for a few hours near the end of the run and to boil down the foots until they show a certain consistency in the sight glass, and then run them to the sewer as soon as the steam is shut off and the vacuum broken. The price of glycerine of course controls this procedure.

71. The glycerine obtained by the process described constitutes the dynamite glycerine of commerce. It is of a pale straw color and requires only subsequent distillation and filtration through bone black to become the water-white, chemically pure glycerine of the pharmacopoeia. Its specific gravity is an important physical characteristic, and is subject to considerable variation. A density of 1.263 at 15° C. is commonly obtained.

A sample from each run of refined glycerine is analyzed for sodium chloride, ash, carbonaceous residue on ignition, and

for acidity, both free and combined, in addition to a determination of the specific gravity. Samples, on standing, tend to accumulate color, due doubtless to an oxidation process of a nature not clearly understood.

72. Chemically Pure Glycerine.—To meet the requirements of the United States Pharmacopoeia, the dynamite grade of glycerine is distilled again and treated with bone black and filtered to make it water white. Sometimes the same object can be obtained by selecting certain portions of the first distillate, treating them with bone black, and filtering. This grade of glycerine is only required to be of 95 per cent. strength and distilled water is added to reduce it.

73. Saponification Crude Glycerine.—All crude glycerines not made by the method previously described are called *saponification crudes*. These include those recovered from the acid saponification and autoclave processes for making soap and candles. Sometimes they are called *candle crude*, or *Twitchell crude*. These crudes are concentrated from lyes containing 15 per cent. of glycerol and are easily distinguished by their low salt content. They have a specific gravity of about 28° Bé., and the best grades will contain 90 per cent. of glycerol. They are refined exactly as are soap-lye crudes and, owing to the absence of salt, are much easier to handle.

74. The chemical examination of the product, not only during the various stages of the refining process, but also at its completion, is a matter of the utmost importance. By this close watching the refiner is warned of changes too delicate for observation, and is thus able to correct in its first stages any abnormal behavior that would deteriorate the final product.

The examination of the refined glycerine not only indicates the care exercised in the refining, but forms the basis for the valuation and sale. The influence exerted by foreign matter in the glycerine on its subsequent use in nitration and the manufacture of dynamite demands a searching chemical and physical examination that is entirely warranted by the danger attending these processes.

CHEMICAL EXAMINATION OF RAW MATERIALS AND PRODUCTS

INTRODUCTION

75. Importance of Chemical Examination.—Every large soap manufactory maintains a chemical laboratory and employs chemists whose duties are to examine all raw materials, thus enabling the purchasing department to avoid losses incident to misrepresentation and to insist on a high grade of material being offered. The chemist analyzes soap and similar products made by competitors, in order to obtain the necessary information whereby his employer is enabled to duplicate it promptly, if desired, at the same or a lower figure. He examines daily the various products that occur in routine factory work and promptly informs the superintendent of conditions requiring modification or elimination. Glycerine recovery cannot be carried on with complete satisfaction without some knowledge of the chemical principles involved in its formation in soap manufacture and its recovery from waste-soap lye. Refined glycerine is sold under a guarantee of its quality, to determine which skill in chemical analysis is necessary. As soap manufactories grow in size and as competition increases, the services of a chemist become more indispensable. It may be truthfully stated that the development of the soap industry to its present proportions would not have been possible without the aid of the chemist.

76. In industrial laboratory work, owing to the quickness with which the information obtained by chemical analysis is desired, many of the analytical methods given in technical treatises are seldom or never used, or only in part. In the routine laboratory work, absolute accuracy, while desired, is not required in every case, it being sufficient that successive

determinations be performed as accurately as the time will permit and that they be uniform, for with uniformity of manufacturing operations, the analytical results must be on a perfectly comparative basis.

EXAMINATION OF SOAP STOCK

77. The following methods of sampling and analysis of soap stock have been taken from the report of the committee appointed by the American Chemical Society, and, contain all the essential features of the methods embodied in the report.

SAMPLING

Tank Cars

1. *Sampling While Loading.*—Sample shall be taken at discharge of pipe where it enters the tank-car dome. The total sample taken shall be not less than 50 pounds and shall be a composite of small samples of about 1 pound each taken at regular intervals during the entire period of loading. The sample thus obtained is thoroughly mixed and uniform 3-pound portions placed in air-tight 3-pound metal containers. At least three such samples shall be put up, one for buyer, one for seller, and the third to be sent to a referee chemist in case of dispute. All samples are to be promptly and correctly labeled and sealed.

2. *Sampling From Car On Track.*[1]—(*a*) When contents are solid:[2] In this case the sample is taken by means of a large tryer measuring about 2 inches across and about $1\frac{1}{2}$ times the depth of the car in length. Several tryerfuls are taken vertically and obliquely toward the ends of the car until 50 pounds are accumulated, when the sample is softened, mixed,

---

[1]Live steam must not be turned into tank cars or coils before samples are drawn, since there is no certain way of telling when coils are free from leaks.

[2]If there is water present under the solid material the fact should be noted and the water estimated separately.

and handled as under 1. In case the contents of the tank car have assumed a very hard condition, as in winter weather, so that it is impossible to insert the tryer and it becomes necessary to soften the contents of the car by means of the closed steam coil (in nearly all tank cars the closed steam coil leaks), or by means of open steam in order to draw a proper sample, suitable arrangements must be made between buyer and seller for the sampling of the car after it is sufficiently softened, due consideration to be given to the possible presence of water in the material in the car as received and also to the possible addition of water during the steaming. The committee knows of no direct method for sampling a hard-frozen tank car of tallow in a satisfactory manner.

(*b*) When contents are liquid: The sample taken is to be a 50-pound composite made up of numerous small samples taken from the top, bottom, and intermediate points by means of a bottle or metal container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths, when the top or stopper is removed and the container allowed to fill. The 50-pound sample thus obtained is handled as under 1.

(*c*) When contents are in a semisolid state, or when stearine has separated from liquid portions: In this case a combination of (*a*) and (*b*) may be used by agreement of the parties or the whole may be melted and procedure (*b*) followed.

Barrels, Tierces, Casks, Drums, and Other Packages

All packages shall be sampled, unless by special agreement the parties arrange to sample a lesser number; but in any case not less than 10 per cent. of the total number shall be sampled. The total sample taken shall be at least 20 pounds in weight for each 100 barrels, or equivalent.

1. *Barrels, Tierces, and Casks.*—(*a*) When contents are solid: The small sample shall be taken by a tryer through the bunghole or through a special hole bored in the head or side for the purpose, with a 1-inch or larger auger. Care should be taken to avoid and eliminate all borings and chips from the sample. The tryer is inserted in such a way as to reach the head of the

barrel, tierce, or cask. The large sample is softened, mixed, and handled according to Tank Cars 1.

(*b*) When contents are liquid: In this case use is made of a glass tube with constricted lower end. This is inserted slowly and allowed to fill with the liquid, when the upper end is closed and the tube withdrawn, the contents being allowed to drain into the sample container. After the entire sample is taken it is thoroughly mixed and handled according to Tank Cars 1.

(*c*) When contents are semi-solid: In this case the tryer or a glass tube with larger outlet is used, depending on the degree of fluidity.

2. *Drums.*—Samples are to be taken as under 1, use being made of the bunghole. The tryer or tube should be sufficiently long to reach the ends of the drum.

3. *Other Packages.*—Tubs, pails, and other small packages not previously mentioned are to be sampled by tryer or tube (depending on fluidity) as already outlined, the tryer or tube being inserted diagonally whenever possible.

4. *Mixed Lots and Packages.*—When lots of tallow or other fats are received in packages of various shapes and sizes, and especially wherein the fat itself is of variable composition, such must be left to the judgment of the sampler. If variable, the contents of each package should be mixed as thoroughly as possible and the amount of the individual samples taken made proportional to the sizes of the packages.

5. *Color.*—It is very important that the color of tallows be kept up to certain standards to secure a uniform product. An arbitrary color system of standards is made in the laboratory by which the melted tallow is compared and given the number which it matches the closest. A very good system of standards can be made from crude glycerine of graduated shades contained in sealed glass tubes. These tubes are of the same kind as those in which the sample is melted. They are numbered or graded from light to dark.

78. Determination of Moisture.—The standard method of determining moisture employs a vacuum oven,

but as only large laboratories are so equipped, a method comparing favorably in results is given.

Method.—Weigh out about 5 grams of the prepared sample into a tared dish. Dry to constant weight in a well-ventilated oven held at a uniform temperature between 105° and 110° C. The thermometer bulb should be close to the dish. Constant weight is attained when successive dryings for 1-hour periods show a loss of not over .05 per cent. The loss should be reported as moisture and volatile matter.

The standard dish is made of glass, shallow, lipped, and beaker form, approximately 6 to 7 centimeters in diameter and 4 centimeters deep.

The air-drying oven is not even approximately accurate for drying and semidrying oils and those of the coconut-oil group. These oils should be tested only in a vacuum oven, for which the method is the same.

A quick qualitative test for much moisture can be made by dropping some of the tallow or oil into the heated bowl of a metal spoon. If a cracking noise or frothing takes place, moisture is present. It is necessary to keep the spoon hot.

79. Determination of Free Fatty Acids.—The determination of free fatty acids is one of the most important tests applied to soap stock, as it gives not only an indication of the value of the stock as a source of glycerine, but of the care exercised in its manufacture and of its origin. The percentage of free fatty acids in soap stock varies, being greater in the summer than in the winter, owing to the fact that the agents of decomposition are more active in the former season. This is shown in Table VI.

As about 10 per cent. of glycerol is theoretically available from soap stocks, a free fatty acidity of 10 per cent. will indicate a loss of 1 per cent. of glycerol, calculated on the basis of the stock, or 10 per cent., calculated on the amount of glycerol theoretically available.

The method of procedure is as follows: Heat the sample sufficiently to melt it, and transfer 5 cubic centimeters to an

Erlenmeyer flask having a wide mouth and a capacity of 250 cubic centimeters; weigh, and add about 50 cubic centimeters of hot, neutral, 95-per-cent. alcohol. Shake well for a few minutes, then add a few drops of alcoholic phenolphthalein solution and titrate with half-normal sodium-hydroxide solution until a permanent pink color is obtained.

TABLE VI

PERCENTAGES OF FREE FATTY ACIDS

Months	Lots	Free Fatty Acid Per Cent.
January	58	4.31
February	55	4.09
March	61	4.27
April	63	5.28
May	47	5.36
June	63	6.39
July	53	8.03
August	81	8.19
September	68	7.28
October	63	7.01
November	54	5.12
December	75	4.58

Calculate free fatty acids in terms of oleic acid the molecular weight of which is 282. One cubic centimeter of $\frac{N}{2}$ $NaOH$ $= .141$ gram of oleic acid. Assuming that x cubic centimeters of $\frac{N}{2}$ $NaOH$ is required for neutralization, the percentage of free fatty acids may be found according to the following formula:

$$\left.\begin{array}{l}\text{Percentage of}\\ \text{free fatty acids}\end{array}\right\} = \frac{x \text{ c. c. } \frac{N}{2} NaOH \times .141 \times 100}{\text{weight taken}}$$

The free-fattty-acid determination, with alcohol as a solvent, is based on the practical insolubility of neutral glycerides in alcohol, while the free fatty acids are soluble.

By measuring a definite volume of the liquid fat, much time is saved, it being a simple matter to ascertain the average weight of 5 cubic centimeters of the soap stock usually examined.

It is customary to calculate free fatty acid to oleic acid except in the cases of palm oil, coconut oil, and palm-kernel oil. The fatty-acid content of palm oil is expressed in terms of palmitic acid while that of coconut and palm-kernel oils is expressed as lauric acid. The molecular weights of palmitic and lauric acids are respectively 256 and 200. They are both monobasic acids.

In order to obtain the best results in making a determination of free fatty acids, 95 per cent. ethyl alcohol, freshly distilled over solid caustic soda, or caustic potash, should be used. However, methyl alcohol and ethyl alcohol denatured with methyl alcohol may be substituted in routine work but they do not give as sharp end points as does ethyl alcohol.

80. Titer Test.—Soap stock of animal origin is bought and sold on the *titer*, by which is meant the highest temperature produced by the latent heat of fusion that is liberated on the solidification of the pure liquid fatty acids obtained from the stock.

To obtain reliable results by whichever modification of the method is used, it is essential that each determination be made under precisely uniform conditions and from fatty acids prepared in the same mnner. This determination may also be applied to cottonseed and coconut oils. For the former stock, it is a reliable index of the soap-making qualities of different samples of oil.

Since all tallows and greases are bought on this test, and since it is by far the most important test that can be given to a stock, it should in all cases be performed where a chemist is employed.

Standard Thermometer.—The thermometer is graduated at zero and in tenths of degrees from 10° C. to 65° C. with one

auxiliary reservoir at the upper end and another between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark is at least 1 centimeter below the 10° mark, and the 10° mark is about 3 or 4 centimeters above the bulb. The length of the thermometer is about 37 centimeters over all. The thermometer has been annealed for 75 hours at 450° C. and the bulb is of Jena normal glass, or its equivalent, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 centimeters long and 6 millimeters in diameter. The stem of the thermometer is 6 millimeters in diameter and made of the best thermometer tubing, with scale etched on the stem. The graduations are clear-cut and distinct, but quite fine. The thermometer must be certified by the U. S. Bureau of Standards.

Glycerine-Caustic Solution.—Dissolve with the aid of heat 250 grams potassium hydroxide in 1,000 cubic centimeters of dynamite glycerine.

Determination.—Heat 75 cubic centimeters of the glycerine-caustic solution to 150° C. and add 50 grams of the melted fat. Stir the mixture well and continue heating until the melt is homogeneous, at no time allowing the temperature to exceed 150° C. Allow to cool somewhat and carefully add 50 cubic centimeters of 30-per-cent. sulphuric acid. Now add hot water and heat until the fatty acids separate out perfectly clear. Draw off the acid water and wash the fatty acids with hot water until free from mineral acid, then filter and heat to 130° C. as rapidly as possible with stirring. Transfer the fatty acids, when cooled somewhat, to a 1″×4″ titer tube, placed in a 16-ounce, wide-mouth bottle of clear glass, fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 revolutions per minute) until the mercury remains stationary for 30 seconds. Allow the thermometer to hang quietly with the bulb in the center of the tube and report as the titer of the fatty acids the highest point to which the mercury rises. The titer should be made at about 20° C.

for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

For American tallows the titer should fall between 41° and 44° C.; for cottonseed oil, between 32° and 33° C.; and for coconut oil, between 23° and 25° C. Cochin oil is usually close to 25° C. The higher the titer the more desirable the material is as a soap stock.

81. Special Tests.—For the proper identification and test for purity of fats and oils, there are numerous tests that can be employed. All the fats and oils have some chemical and physical properties that are constant between certain limits. The variations are due to locality of origin, method of extraction, refining, etc. Among these constants are the iodine value and the saponification value.

82. Iodine Value.—Fats and saponifiable oils have the property of absorbing iodine chloride because of the unsaturated fatty acids and glycerides which they contain. The percentage of iodine chloride which it absorbs, expressed in terms of iodine, is called the *iodine value* of the compound.

WIJS METHOD FOR DETERMINATION OF IODINE VALUE

83. Preparation of Reagents.—*Wijs Iodine Solution.*—(1) Dissolve separately 7.9 grams of iodine trichloride and 8.7 grams of iodine in glacial acetic acid on the water bath, taking care that the solutions do not absorb moisture. The two solutions are then poured into a 1,000 cubic centimeter flask, which is then filled up to the mark with glacial acetic acid.

Or (2) dissolve 6.5 grams of resublimed iodine in 1 liter of C. P. glacial acetic acid and pass in washed and dried chlorine gas until the original sodium-thiosulphate titration of the solution is just doubled. This solution is then preserved in amber glass-stoppered bottles, sealed with paraffin until ready for use.

$\frac{N}{10}$ *Sodium-Thiosulphate Solution.*—Dissolve 24.8 grams of C. P. sodium thiosulphate and dilute with water to 1 liter at the temperature at which the titrations are to be made.

Starch Paste.—Boil 1 gram of starch in 200 cubic centimeters of distilled water for 10 minutes and cool to room temperature.

Potassium-Iodide Solution.—Dissolve 150 grams of potassium iodide in water and make up to 1 liter.

$\frac{N}{10}$ *Potassium-Bichromate Solution.*—Dissolve 4.903 grams of C. P. potassium bichromate in water and make the volume up to 1 liter at the temperature at which titrations are to be made. One cubic centimeter = .012685 gram iodine.

Standardization of Sodium-Thiosulphate Solution.—Place 20 cubic centimeters of the potassium-bichromate solution, to which has been added 10 cubic centimeters of the solution of potassium iodide, in a glass-stoppered flask. Add to this 5 cubic centimeters of strong hydrochloric acid. Dilute with 100 cubic centimeters of water, and allow the $\frac{N}{10}$ sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the $\frac{N}{10}$ sodium-thiosulphate solution until the blue color just disappears.

Determination.—Weigh accurately from .10 to .50 gram, depending on the iodine number, of the melted and filtered sample into a clean, dry, 16-ounce glass-stoppered bottle containing 15 to 20 cubic centimeters of carbon tetrachloride or chloroform. Add 25 cubic centimeters of iodine solution from a pipette, allowing the latter to drain for a definite time. The excess of iodine should be from 50 to 60 per cent. of the amount added, that is, from 100 per cent. to 150 per cent. of the amount absorbed. Moisten the stopper with a 10-per-cent. potassium-iodide solution to prevent loss of iodine or chlorine, but guard against an amount sufficient to run down inside the bottle. Let the bottle stand in a dark place for ½ hour at a uniform temperature. At the end of that time add 20 cubic centimeters of 10-per-cent. potassium-iodide solution and 100 cubic centimeters of distilled water. Titrate the iodine

with $\frac{N}{10}$ sodium-thiosulphate solution, which is added gradually with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently so that any iodine remaining in solution in the tetrachloride or chloroform may be taken up by the potassium-iodide solution. Conduct two determinations on blanks, which must be run in the same manner as the sample except that no fat is used in the blanks. Slight variations in temperature quite appreciably affect the volume of the iodine solution, as acetic acid has a high coefficient of expansion. It is, therefore, essential that the blanks and determinations on the sample be made at the same time. The number of cubic centimeters of standard thiosulphate solution required by the blank, less the amount used in the determination, gives the thiosulphate equivalent of the iodine absorbed by the amount of sample used in the determination. Calculate to centigrams of iodine absorbed by 1 gram of sample.

To illustrate the application of the Wijs method, assume that, in making a determination, .1355 gram of linseed oil was weighed and treated with 25 cubic centimeters of the iodine solution. In a blank test 61.2 cubic centimeters of sodium-thiosulphate solution were needed for the iodine solution. In the determination 41.1 cubic centimeters of sodium-thiosulphate solution were required to titrate the excess of iodine. Therefore the iodine absorbed by the oil was equivalent to 20.1 cubic centimeters of sodium-thiosulphate solution: 20 cubic centimeters of the bichromate solution = .2537 gram iodine. It required 20.8 cubic centimeters of the sodium-thiosulphate solution in the standardization to titrate the 20 cubic centimeters of bichromate solution. Therefore,

20.8 cubic centimeters of sodium thiosulphate = .2537 gram iodine and,

20.1 cubic centimeters of sodium thiosulphate = .24516 gram iodine.

$$\frac{.24516 \times 100}{.1355} = 181, \text{ the iodine value of the linseed oil used.}$$

84. Saponification Number.—The number of milligrams of potassium hydroxide required for the complete saponification of 1 gram of fat or oil is called the *saponification number*, or *Koettstorfer number*. The reagents required are $\frac{N}{2}$ hydrochloric acid, carefully standardized, and a solution of alcoholic potassium hydroxide, prepared as follows: Dissolve 40 grams of pure potassium hydroxide in 1 liter of 95-per-cent. redistilled alcohol. The alcohol should be redistilled from potassium hydroxide over which it has been standing for some time, or with which it has been boiled for some time, using a reflux condenser. The solution must be clear and the potassium hydroxide free from carbonate.

Determination.—Weigh accurately about 5 grams of the filtered sample into a 250 to 300 cubic centimeter Erlenmeyer flask. Pipette 50 cubic centimeters of the alcoholic potassium-hydroxide solution into the flask, allowing the pipette to drain for a definite time. Connect the flask with an air condenser and boil until the fat is completely saponified (about 30 minutes). Cool and titrate with the $\frac{N}{2}$ hydrochloric acid, using phenolphthalein as an indicator. Calculate the Koettstorfer number (mg. of potassium hydroxide required to saponify 1 gram of fat). Conduct two or three blank determinations, using the same pipette and draining for the same length of time as above.

To illustrate the application of the method, assume that, in making a determination, 1.4812 grams of olive oil was weighed out and saponified with 25 cubic centimeters of alcoholic-potash solution, and that 15.2 cubic centimeters $\frac{N}{2}$ *HCl* was required to titrate back the excess of alkali. The blank required 25.4 cubic centimeters $\frac{N}{2}$ *HCl*; therefore, 10.2 cubic centimeters represents the alkali absorbed.

Calculation of Results.—

$$10.2 \times .02805 = .28611 \text{ g. } KOH = 286.11 \text{ mg. } KOH$$

$$286.11 \div 1.4812 = 193.2, \text{ saponification number}$$

Table VII gives the iodine and saponification values of some of the more common oils.

TABLE VII

IODINE AND SAPONIFICATION VALUES OF COMMON OILS

Name of Oil	Iodine Value	Saponification Value
Castor	87 to 93	183 to 186
Coconut	8.4 to 9.3	246 to 260
Corn	119 to 122	188 to 193
Cottonseed	111 to 115	193 to 195
Linseed	179 to 209	192 to 195
Olive	86 to 90	185 to 196
Palm	51 to 53	196 to 205
Palm-kernel	13 to 17	242 to 250
Peanut	96 to 103	190 to 196
Rape	99 to 103	170 to 179
Soya-bean	138 to 142	195
Tung	144 to 159	193
Tallow, beef	40.5 to 42	193 to 200
Tallow, mutton	34 to 35	192 to 195

ANALYSIS OF ROSIN

85. Determination of Unsaponifiable Matter.—The only chemical test commonly applied to rosin is the determination of the unsaponifiable matter, which increases, as previously stated, as the quality of the rosin decreases. The grading accorded the barrel from which the sample is taken is determined by comparing with standard cubes a cube cut from the sample, with dimensions equal to those of the standard. Care should be taken to have the sample cube representative of the quality of rosin in the barrel. The unsaponifiable matter present is determined in the same manner as the unsaponifiable matter in glyceride stock.

86. Comparison With Standards.—Rosin of a given grade should correspond in color and clearness with the

standard cube of the same grade. The standards should be renewed from time to time, as they tend to bleach on exposure and to lose the cube shape through softening. In comparing samples with the standards, strict uniformity of dimensions and exposure to light must be observed.

ANALYSIS OF SODA ASH

87. Determination of Sodium Carbonate.—In order to determine the amount of sodium carbonate present in soda ash, weigh 1 or 2 grams of the sample into a 500-cubic-centimeter flask and dissolve in water; add a few drops of phenolphthalein as indicator. Run in from a burette an accurately measured excess of half-normal sulphuric acid and boil to expel all traces of carbon dioxide. Titrate the excess of acid with half-normal caustic soda. The solutions are equal and are known in terms of the various sodium compounds. The weight of sodium carbonate corresponding to the number of cubic centimeters of half-normal sulphuric acid required to neutralize the soda ash multiplied by 100 is divided by the weight of alkali taken, and the result is the percentage of actual anhydrous sodium carbonate present in the soda ash.

88. Determination of Total Alkali.—To determine the total alkali present, dissolve 10 grams of the soda ash in about 150 cubic centimeters of warm distilled water and dilute to 1 liter. Remove 50 cubic centimeters of this solution to a beaker and titrate with half-normal sulphuric acid, using methyl orange as indicator. Since 1 cubic centimeter of half-normal acid is equivalent to .03082 gram of Na_2O, the percentage of Na_2O in the soda ash will be found by multiplying the number of cubic centimeters of half-normal acid required by $.03082 \times 20 \times 100$ and dividing the result by 10 (the weight of the sample taken).

ANALYSIS OF COMMERCIAL CAUSTIC SODA

89. Determination of Total Alkali.—The determination of the total amount of alkali present in commercial caustic soda is carried out exactly as explained for the determination of the total alkali of soda ash. The percentage of total alkali is expressed in terms of sodium oxide.

90. Determination of Sodium Hydroxide.—To determine the actual amount of sodium hydroxide in commercial caustic soda, weigh out about 5 grams of the sample from a glass-stoppered weighing bottle and as quickly as possible add distilled water that has previously been boiled and cooled. Transfer to a 250-cubic-centimeter graduated flask, make up to the mark and mix thoroughly. Take out 25 cubic centimeters and dilute with 50 cubic centimeters of the same distilled water. Add 3 or 4 drops of phenolphthalein solution and titrate slowly with $\frac{N}{5}$ hydrochloric acid, stirring vigorously until only a faint pink remains, and note the reading. Then add 1 or 2 drops of methyl-orange solution and resume the titration with the same acid until only a faint pink remains.

Twice the amount of acid used in the methyl-orange titration equals the amount of sodium carbonate present. The result obtained when this amount is subtracted from the total acid used indicates the amount of sodium hydroxide present.

$$1 \text{ c.c. } \frac{N}{5}\ HCl = .01061 \text{ g. } Na_2CO_3$$

$$1 \text{ c.c. } \frac{N}{5}\ HCl = .008012 \text{ g. } NaOH$$

Calculate the amount of each present in 250 cubic centimeters.

The theory on which the method is based is, that in mixtures of caustic and carbonate-of-soda solutions, the entire caustic and only one-half the carbonate are neutralized in the presence of phenolphthalein as an indicator, when the acid is added slowly to the cold solution and the latter well stirred. This is due to the formation of sodium bicarbonate ($NaHCO_3$), which

does not react with phenolphthalein but gives a complete end point with methyl orange. Therefore, the safe use of the method depends on losing none of the carbonic acid.

91. Determination of Sodium Chloride.—The lower grades of caustic soda contain salt. To determine the salt, take 25 cubic centimeters of the sample solution, add a drop of methyl orange, and make slightly acid with nitric acid. Add a slight excess of pure calcium carbonate, stir well and filter. Wash with hot water, add a few drops of a 5-per-cent. potassium-chromate solution and titrate to a slight red color with $\frac{N}{10}$ silver-nitrate solution.

1 c. c. $\frac{N}{10}$ silver-nitrate solution = .005868 g. sodium chloride.

To illustrate the method of using the results obtained by carrying out the methods of analysis for sodium hydroxide, sodium carbonate, and sodium chloride, assume that 58.4 c. c. of $\frac{N}{5}$ *HCl* were required for the phenolphthalein titration, .66 c. c. for the methyl-orange titration, and 3.7 c. c. of the $\frac{N}{10}$ silver-nitrate solution for the sodium-chloride determination.

Then, 58.4 c. c. $\frac{N}{5}$ *HCl* for phenolphthalein

.6 c. c. $\frac{N}{5}$ *HCl* for methyl orange

59.0

1.2

57.8 c. c. = sodium hydroxide

1.2 c. c. = sodium carbonate

1 c. c. $\frac{N}{5}$ *HCl* = .008012 g. sodium hydroxide

1 c. c. $\frac{N}{5}$ *HCl* = .01061 g. sodium carbonate

$$\frac{57.8 \times .008012 \times 100}{.5 \text{ (wt. of sample)}} = 92.62 \text{ per cent.}$$

$$\frac{1.2 \times .01061 \times 100}{.5 \text{ (wt. of sample)}} = 2.55 \text{ per cent.}$$

$$1 \text{ c. c. } \frac{N}{10} AgNO_3 = .005846 \text{ g. of sodium chloride}$$

$$\frac{3.7 \times .005846 \times 100}{.5 \text{ (wt. of sample)}} = 4.32 \text{ per cent.}$$

From the foregoing results, the analysis would be reported as:

	Per Cent.
Sodium hydroxide	92.62
Sodium carbonate	2.55
Sodium chloride	4.32
	99.49

This expressed in percentage of Na_2O and as degrees would make it of the 74° grade.

92. Caustic potash and pearl ash are examined in the same manner. If the quantity of potash purchased warrants the work, the percentage of caustic soda, sodium carbonate, potassium chlorides, and the alkali sulphates may be determined. These compounds are present as impurities.

ROUTINE CHEMICAL EXAMINATION OF KETTLE-ROOM PRODUCTS

ANALYSIS OF WASTE SOAP LYE

93. Determination of Total Alkali.—In order to determine the total alkali present in the waste soap lye, transfer 10 cubic centimeters of waste lye into a clean, 500-cubic-centimeter flask by means of a pipette. Dilute with 150 cubic centimeters of water, add phenolphthalein as indicator, and run in from a burette sufficient half-normal sulphuric acid to discharge the pink color. Boil to expel carbon dioxide and titrate back with seminormal caustic soda.

Illustration.—*Long Method.*—The amount of $\frac{N}{2} H_2SO_4$ required for neutralization is 1.94 cubic centimeters; 1 cubic centimeter of $\frac{N}{2} H_2SO_4$ equals .02 gram of $NaOH$. Total alkali, estimated as $NaOH$, equals $\frac{1.94 \times .02 \times 100}{10} = .388$ gram of $NaOH$ in 100 cubic centimeters of liquor.

Short Method.— CUBIC CENTIMETERS

Total amount of $\frac{N}{2}$ H_2SO_4 used is 5.90

Amount of $\frac{N}{2}$ $NaOH$ used for titrating excess of $\frac{N}{2}$ H_2SO_4 is 3.96

Amount of $\frac{N}{2}$ H_2SO_4 absorbed..... 1.94

The total alkali, estimated as $NaOH$, is $1.94 \times .2 = .388$ gram of $NaOH$ in 100 cubic centimeters of liquor.

It will be observed that these methods give the percentage of alkali by volume; the percentage by weight would be slightly less.

94. Determination of Sodium Chloride.—In order to determine the sodium chloride contained in the waste soap lye, transfer 5 cubic centimeters of waste lye into a 100-cubic-centimeter beaker by means of a pipette and dilute with 50 cubic centimeters of distilled water. Mix well and transfer 5 cubic centimeters of the diluted lye to a 4-inch porcelain evaporating dish. Now add dilute nitric acid to a slight excess, then pure calcium carbonate. Stir the contents of the dish, filter, wash with hot water and titrate the filtrate with decinormal silver-nitrate solution, using postassium chromate as indicator. Calculate the percentage of sodium chloride as if 5 grams of lye had been taken for analysis.

ILLUSTRATION.—Amount of waste lye taken is 5 cubic centimeters; amount of $\frac{N}{10}$ $AgNO_3$ required is 20.5 cubic centimeters.

$$\frac{20.5 \times .005846 \times 100}{5} = 2.35 \text{ per cent. of } NaCl \text{ (by volume)}$$

The true percentage by weight is found by dividing the preceding result by the specific gravity of the waste lye.

95. Determination of Glycerol.—As the glycerol determination requires some time, it is only done when special information as to the glycerol content of a particular lye is desired, or when crude glycerine is being purchased, on glycerol content, for refining. The analytical methods used industrially are based on the complete oxidation of glycerol to carbon dioxide and water. Potassium bichromate and sulphuric acid are used to effect the oxidation. In another, the

acetin process, the quantitative determination of the glycerol is based on its transformation into glyceryl triacetin, in accordance with the following equation:

$$2C_3H_5(OH)_3+3(CH_3\cdot CO)_2\cdot O=2C_3H_5(CH_3COO)_3+3H_2O$$

This method, when carried out by a chemist who is skilled in its operation, gives the most accurate results. One great source of error in all the oxidation methods for the determination of glycerol is the danger of oxidizing organic impurities that are incompletely removed from the solution. As a result, all oxidation methods give uniformly high results. In the acetin method, only the glyceride is susceptible to the action of the acetic anhydride.

96. Acetin Method.—When the **acetin method** is employed, about 1½ grams of crude glycerine is heated with 7 or 8 grams of acetic anhydride and 3 grams of anhydrous sodium acetate. The function of the last reagent is to absorb water. The mixture is gently boiled for 1½ hours in a flask provided with a water-cooled, reflux condenser. At the expiration of this period, cool the contents of the flask and introduce 50 cubic centimeters of water through the condenser. With the condenser attached, agitate with slight warming until the oily matter in the bottom of the flask has dissolved. Filter when cool, and to the filtrate add a few drops of phenolphthalein. Run in dilute caustic soda (20:1,000) from a burette until just neutral (until the yellow color just changes to reddish yellow). The free acid is thus neutralized. Now run in from a burette a measured quantity, usually about 25 cubic centimeters, of caustic-soda solution of known strength (about twice normal or a little stronger). Heat the contents of flask on a water bath and titrate the excess of caustic soda with normal hydrochloric acid. The percentage of glycerol present, as calculated from the amount of sodium hydroxide used to saponify the triacetin, will be evident from the following calculation:

ILLUSTRATION.—The amount of sodium-hydroxide solution added after neutralization was 27.15 cubic centimeters. Assume that one cubic centimeter of the sodium-hydroxide solution used equals 2.42 cubic centi-

meters of normal hydrochloric acid. Therefore, 27.15 cubic centimeters $\times 2.42 = 65.70$ cubic centimeters, the equivalent of 27.15 cubic centimeters of sodium hydroxide in normal hydrochloric acid.

After saponification, 33.2 cubic centimeters of normal hydrochloric acid was required to neutralize the excess of sodium hydroxide; 65.7 cubic centimeters less 33.2 cubic centimeters equals 32.5 cubic centimeters of normal hydrochloric acid, which is equivalent to the sodium hydroxide required for the saponification of the triacetin. One cubic centimeter of normal acid equals .03069 gram of glycerol, 32.5 cubic centimeters of normal acid equals .99742 gram of glycerol; weight taken for analysis equals 1.2501 grams.

$$\frac{.99742 \times 100}{1.2501} = 79.78 \text{ per cent. glycerol present}$$

97. Bichromate Oxidation Method.—The bichromate oxidation method is based on the fact that 1 gram of glycerol is completely oxidized to carbon dioxide by 7.4564 grams of potassium bichromate in the presence of sulphuric acid. It does not require the skill of manipulation of the acetin method, but unfortunately it does not give as accurate results because of the oxidation of organic matter, other than glycerol, which may also be present. The following reagents are required:

Potassium bichromate.—The very purest salt obtainable is powdered and dried at 140° C. and kept in a tight-fitting glass-stoppered bottle.

Mohr's salt.—$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.—Dissolve 3.7282 grams of the dry $K_2Cr_2O_7$ in 30 c. c. of water, add 50 cubic centimeters of 50 per cent. H_2SO_4 and to the cold undiluted solution add a moderate excess of Mohr's salt from a tared weighing bottle. Titrate back the excess of Mohr's salt with the $K_2Cr_2O_7$ solution described later. Calculate the value of the Mohr's salt in terms of $K_2Cr_2O_7$.

Standard $K_2Cr_2O_7$ Solution.—Dissolve 7.4564 grams $K_2Cr_2O_7$ in 1,000 cubic centimeters water. 1 cubic centimeter contains .0074564 gram $K_2Cr_2O_7 = .001$ gram glycerol.

Basic Lead Acetate.—Dissolve 235 grams of lead acetate in 1,000 cubic centimeters of water; boil, and stir in 165 grams of litharge. Boil and stir 15 minutes.

Silver Acetate.—A saturated solution is prepared at ordinary temperatures (about 20° C.).

Dilute Sulphuric Acid.—Add 150 cubic centimeters H_2SO_4 to 850 cubic centimeters of water, with the usual precautions.

The method of procedure is to weigh out 20 grams of the crude glycerine, make up to 250 cubic centimeters, and mix thoroughly. Pipette off 25 cubic centimeters into a 50-cubic-centimeter beaker and add a slight excess of the basic acetate-of-lead solution. Wash several times by decantation, decanting through a filter into a 250-cubic-centimeter graduated flask. Pour precipitate on the filter and wash thoroughly. Add 12 cubic centimeters saturated silver-acetate solution and a slight excess of dilute sulphuric acid (about 5 cubic centimeters) and make it up to the mark with .2 cubic centimeter excess to allow for volume of precipitate. Mix well. Filter through a dry filter and reject first portion, collecting the balance in a glass-stoppered 250-cubic-centimeter flask.

Weigh out 1.8641 grams of the $K_2Cr_2O_7$ into a 150-cubic-centimeter beaker (previously cleaned with $K_2Cr_2O_7$ and H_2SO_4 solution and washed with distilled water). Add 25 cubic centimeters distilled water and then 25 cubic centimeters of the clear filtrate to be tested and stir until the $K_2Cr_2O_7$ is dissolved. Add with constant stirring 25 cubic centimeters of concentrated H_2SO_4, transfer to a steam bath and oxidize for 30 minutes, keeping the beaker covered with an absolutely clean watch glass. Remove from the bath and add a slight excess of Mohr's salt from a tared weighing bottle and titrate back the excess with the standard $K_2Cr_2O_7$ solution, using potassium ferricyanide on a white spot plate as an indicator.

Calculation of Results.—Because of the manner in which the 20-gram sample of crude glycerine was diluted, namely, the 20 grams to 250 cubic centimeters and 25 cubic centimeters of this solution to 250 cubic centimeters, the 25-cubic-centimeter portion of the latter solution, that was treated with potassium bichromate, contains only .2 gram of crude glycerine, or $\frac{1}{100}$ of the original sample. Assume that in this particular analysis, 1.8641 grams of solid $K_2Cr_2O_7$ are added to .2 gram of the crude glycerine, in order to oxidize the glycerol that it contains. This quantity of $K_2Cr_2O_7$ is more than enough to oxidize the glycerol in the .2-gram sample, since

7.4564 grams $K_2Cr_2O_7$ will oxidize 1 gram of glycerol. Therefore $K_2Cr_2O_7$ will be present in excess and the exact excess is determined by means of Mohr's salt and the standard $K_2Cr_2O_7$ solution. Assume that of the particular Mohr's salt used, 8.015 grams were equivalent to 1 gram of $K_2Cr_2O_7$, that 5.4892 grams of Mohr's salt were added to reduce the excess $K_2Cr_2O_7$, and that 7.3 cubic centimeters of the standard $K_2Cr_2O_7$ solution were required to oxidize the excess of Mohr's salt added.

$$1 \text{ c. c. } K_2Cr_2O_7 \text{ solution} = .0074564 \text{ g. } K_2Cr_2O_7$$

$$7.3 \text{ c. c. } K_2Cr_2O_7 \text{ solution} = .0544 \text{ g. } K_2Cr_2O_7$$

$$1 \text{ g. } K_2Cr_2O_7 = 8.015 \text{ g. Mohr's salt}$$

$$.0544 \text{ g. } K_2Cr_2O_7 = .436 \text{ g. Mohr's salt}$$

The excess of Mohr's salt used is then .436 gram. The total quantity of Mohr's salt used was 5.4892 grams. Then,

$$5.4892 - .436 = 5.0532 \text{ grams}$$

of Mohr's salt actually used up in reducing the excess $K_2Cr_2O_7$.

$$1 \text{ g. Mohr's salt} = .124 \text{ g. } K_2Cr_2O_7$$

5.0532 g. Mohr's salt = .6265 g. $K_2Cr_2O_7$, which represents the excess. Then,

$1.8641 - .6265 = 1.2376$ g. $K_2Cr_2O_7$ actually required to oxidize the glycerol in the .2-gram sample.

$$1 \text{ g. } K_2Cr_2O_7 = .134 \text{ g. glycerol}$$

$$1.2376 \times .134 = .1658 \text{ g. glycerol in the sample}$$

$$\frac{.1658 \times 100}{.2} = 82.9 \text{ per cent. glycerol in the sample}$$

This is a modification of the general method, but has a great advantage in using the dry salts in place of the concentrated solutions. It gives excellent results.

Glycerol in Filter-Press Cake.—Extract 10 grams of the cake five or six times with boiled, distilled water, using about 350 cubic centimeters in all. Evaporate the filtrate to 75 cubic centimeters; purify with lead acetate, silver acetate, and sulphuric acid by the method just given. The solution is made up to exactly 250 cubic centimeters and one-fifth or one-tenth taken for oxidation. The rest of the analysis is carried out as directed in the method already given.

Glycerol in Recovered Salt.—Extract a 10-gram sample of the salt with an alcohol-ether (1:3) solution. Evaporate the

extract to expel the alcohol and ether. This is done on a steam bath and may be hastened by adding small amounts of water after the extract has been concentrated to a small volume. The alcohol will evaporate quicker if this is done and there is less danger of losing glycerine. When the alcohol has been removed, the extract is diluted, purified, and oxidized by the method given.

SOAP ANALYSIS AND THE INTERPRETATION OF RESULTS

98. Assume that a cake of soap made by the boiled or settled process analyzed as follows:

	Per Cent.
Water	31.27
Fatty anhydride	37.57
Rosin anhydride	20.28
Combined alkali	6.57
Free caustic alkali	none
Free carbonated alkali	2.51
Salt	.21
Unsaponifiable	1.08
Undetermined	.51
	100.00

Then combining the ingredients according to their existing state in the soap, the analysis would appear as follows:

			Per Cent.
Water			31.27
Soap	Combined alkali as Na_2O	6.57	64.42
	Fatty anhydrides	37.57	
	Rosin anhydrides	20.28	
Carbonated alkali, Na_2CO_3			2.51
Salt			.21
Unsaponifiable			1.08
Undetermined (glycerol, etc.)			.51
			100.00

99. It will be assumed that the sample analyzed is a fairly fresh piece of soap, not having undergone much dry-

ing. Settled rosin soap fresh from the cutting table is known to contain from 30 to 35 per cent. of water. The sample is further confirmed as one of a settled soap by the analysis, which shows no free caustic, the absence of much glycerol, and the low percentage of unsaponifiable matter. It is also possible to tell from the appearance of the sample whether the soap is a cold-process or a settled soap. Thus, if it has a broad, open texture resulting from the slow crystallization of

TABLE VIII

ANALYSES OF VARIOUS LAUNDRY SOAPS

Ingredients	1	2	3	4	5	6	7
	Per Cent. of Each Ingredient						
Water	26.30	26.37	29.68	70.14	71.59	28.67	31.18
Fatty anhydride	33.52	30.77	34.23	7.20	8.63	41.69	37.57
Rosin anhydride	24.57	28.89	18.34	none	none	15.06	20.28
Combined alkali	6.54	7.21	6.21	1.33	1.53	6.87	6.57
Free $NaOH$	trace	none	.04	none	.12	none	.02
Free Na_2CO_3	2.14	2.53	2.94	7.87	5.26	2.23	2.01
Sodium silicate	1.24	1.47	2.90	none	none	none	none
Salt	.35	.19	.23	11.28	10.14	.30	.21
Unsaponifiable	3.08		5.36				1.08
Insoluble	2.26	2.49	.07		.23	.48	.08

the sodium stearate in a menstruum of sodium oleate and sodium resinate, it is safe to say that the soap has not been crutched. If the soap is homogeneous in texture, with no marked crystallization, it has been crutched, in which process the texture arising from the slow cooling of the unfilled soap in the frames is broken up by the intimate mixing in the crutcher of the soap formed from fatty acids of different melting points. In Table VIII are given the analyses of various laundry soaps.

CHEMICAL EXAMINATION OF REFINED GLYCERINE

100. Determination of Salt.—To determine the amount of salt in a sample of refined glycerine, 100 cubic centimeters of the sample is diluted with 200 cubic centimeters of water and titrated directly with $\frac{N}{10}$ $AgNO_3$, using potassium chromate as an indicator. For all practical purposes, the weight of 100 cubic centimeters of glycerine is taken as 126 grams.

101. Determination of Ash.—To determine the ash present, weigh out 25 grams of glycerine on the coarse balance into a weighed platinum dish. Heat carefully to ignition and allow combustion to proceed. Expel all carbonaceous matter with a strong Bunsen-burner flame, taking care to lose no salt by volatilization or decrepitation. Cool and weigh on the fine balance. Calculate the percentage of ash as in the preceding case.

102. Higher Fatty Acids.—Pass a stream of nitrogen tetroxide through a portion of the glycerine that is diluted with twice its volume of distilled water and contained in a test tube. After this operation place the test tube on a steam bath and heat for 2 hours. Glycerine that is to be used for the manufacture of nitroglycerine should give no precipitate, either on dilution or later in the operation. Glycerine that will stand this test may be considered free from higher fatty acids.

103. Neutrality.—A glycerine may be considered neutral if, when 50 grams is diluted with twice its weight of distilled water and a few drops of an alcoholic solution of phenolphthalein are added, not more than 1 cubic centimeter of $\frac{N}{4}$ sulphuric-acid or sodium-hydroxide solution is required to produce a change in color.

104. Specific Gravity.—Next to the quality of the glycerine, the specific gravity is the most important test, and

this test requires care and skill for its accurate determination. The instrument used for making the specific-gravity determination is called a *picnometer*. As shown by Fig. 13, it consists of a flask *a* the volume of which is known and which is fitted with a capillary tube *b*. This tube is capped by a glass cap *c*. The joint between the cap and the capillary tube is air-tight because of the fact that the outside of the tube *b* and the inside of *c* have been ground to a perfect fit. This is known as a ground-glass joint. The flask *a* also contains a thermometer *d* which is made to fit tightly by means of the ground-glass joint which it forms with *a* at *e*.

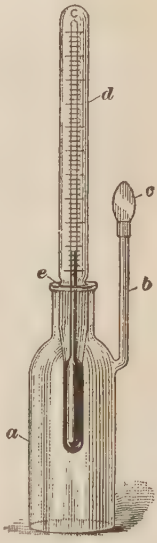


FIG. 13

The sample of glycerine in a glass-stoppered flask is cooled to a temperature of 10 to 12° C. and then transferred to the picnometer, which must be filled. The thermometer is then inserted and seated and the cap *c* removed. The picnometer is placed at once in a bath of ice water up to its neck. The bath is kept at a temperature of 12 to 13° C. by the ice and is well stirred to allow the temperature to rise slowly. The object is to get the temperature of the contents of the picnometer to equal the temperature of the bath at 15.5° C. When this equilibrium is reached, the excess of glycerine is carefully removed from the tip of the capillary tube and the cap put on. The picnometer is then taken from the bath, wiped off until absolutely dry, and allowed to stand in the balance room. When it has reached room temperature it is weighed.

The total weight of the picnometer and glycerine minus the weight of the picnometer, gives the weight of a certain known volume of glycerine. The operation is now carried out with pure water under the same conditions. Then the weight of the glycerine divided by the weight of an equal volume of water at the same temperature gives the specific gravity of the glycerine. Table IX gives the specific gravities of aqueous solutions of glycerine as determined by Gerlach and Skalweit.

TABLE IX

SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF CHEMICALLY PURE GLYCERINE

Per Cent. Glycerol	Gerlach		Skalweit	Per Cent. Glycerol	Gerlach		Skalweit
	Sp. Gr. 15° C.	Sp. Gr. 20° C.	Sp. Gr. 15° C.		Sp. Gr. 15° C.	Sp. Gr. 20° C.	Sp. Gr. 15°
0	1.0000	1.0000	1.0000	51			1.1318
1			1.0024	52			1.1346
2			1.0048	53			1.1374
3			1.0072	54			1.1402
4			1.0096	55	1.1430	1.4150	1.1430
5			1.0120	56			1.1458
6			1.0144	57			1.1486
7			1.0168	58			1.1514
8			1.0192	59			1.1542
9			1.0216	60	1.1570	1.1550	1.1570
10	1.0245	1.0235	1.0240	61			1.1599
11			1.0265	62			1.1628
12			1.0290	63			1.1657
13			1.0315	64			1.1686
14			1.0340	65	1.1711	1.1685	1.1715
15			1.0365	66			1.1743
16			1.0390	67			1.1771
17			1.0415	68			1.1799
18			1.0440	69			1.1827
19			1.0465	70	1.1850	1.1820	1.1855
20	1.0490	1.0480	1.0490	71	1.1878	1.1847	1.1882
21			1.0516	72	1.1906	1.1874	1.1909
22			1.0542	73	1.1934	1.1901	1.1936
23			1.0568	74	1.1962	1.1928	1.1963
24			1.0594	75	1.1990	1.1955	1.1990
25	1.0620	1.0610	1.0620	76	1.2018	1.1982	1.2017
26			1.0646	77	1.2046	1.2009	1.2044
27			1.0672	78	1.2074	1.2036	1.2071
28			1.0698	79	1.2102	1.2063	1.2098
29			1.0724	80	1.2130	1.2090	1.2125
30	1.0750	1.0740	1.0750	81	1.2157	1.2117	1.2152
31			1.0777	82	1.2184	1.2144	1.2179
32			1.0804	83	1.2211	1.2171	1.2206
33			1.0831	84	1.2238	1.2198	1.2233
34			1.0858	85	1.2265	1.2225	1.2260
35	1.0885	1.0875	1.0885	86	1.2292	1.2252	1.2287
36			1.0912	87	1.2319	1.2279	1.2314
37			1.0939	88	1.2346	1.2306	1.2341
38			1.0966	89	1.2373	1.2333	1.2368
39			1.0993	90	1.2400	1.2360	1.2395
40	1.1020	1.1010	1.1020	91	1.2425	1.2386	1.2421
41			1.1047	92	1.2451	1.2412	1.2447
42			1.1074	93	1.2476	1.2438	1.2473
43			1.1101	94	1.2501	1.2464	1.2499
44			1.1128	95	1.2526	1.2490	1.2525
45	1.1155	1.1145	1.1155	96	1.2552	1.2516	1.2550
46			1.1182	97	1.2577	1.2542	1.2575
47			1.1209	98	1.2602	1.2568	1.2600
48			1.1236	99	1.2628	1.2594	1.2625
49			1.1263	100	1.2653	1.2620	1.2650
50	1.1294	1.1280	1.1290				

SPECIFICATIONS FOR GLYCERINE

105. The principal specifications for chemically pure glycerine are that it shall be water-white in color, of very slight odor, and have a specific gravity at 25° C. of 1.249; it must be neutral to litmus in a 1:20 water solution; it must not have a total residue on ignition of more than .0105 per cent., of which not more than .007 per cent. of the whole must be mineral matter, and a total chlorine content of more than .001 per cent. calculated as sodium chloride.

106. The following specifications have been prepared by a large consumer for the purchase of dynamite glycerine:

1. Specific gravity. Not less than 1.262 at $\frac{15.5°}{15.0°}$ C.
2. Odor. Slight. No bad odor.
3. Color. Not darker than straw color.
4. Acidity. When 50 cubic centimeters of the glycerine plus 10 cubic centimeters of distilled water free from carbon dioxide are mixed and about ½ cubic centimeter of phenolpthalein indicator (5 g. per liter of 50-per-cent. alcohol) used, it shall not require more than .3 cubic centimeter of normal hydrochloric acid nor more than .3 cubic centimeter of normal sodium-hydroxide solution for neutralization.
5. Ash not over .1 per cent.
6. Chlorine. Not over .01 per cent. chlorine as calculated from a volumetric determination of the chlorine in the aqueous solution of the residue left on ignition.
7. Nitration and separation. When 15 grams are nitrated in a glass vessel with 70 cubic centimeters of a mixture consisting of 37-per-cent. pure nitric acid of 1.5 specific gravity and 63-per-cent. pure sulphuric acid of 1.845 specific gravity, at a temperature not allowed to exceed 20° C., and the whole poured into a glass cylinder of 1½ inches internal diameter, the nitroglycerine should separate so that the line of demarcation will be clear, and there should be practically no so-called flocculent matter present.